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Correlated theory of linear optical absorption of octacene and nonacene

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Abstract. The technological importance of higher acenes has led to resurgence of interest in synthesizing higher acenes such as octacene, nonacene etc. Recently, Tönshoff and Bettinger [2010 *Angew. Chem. Int. Ed.* **49** 4125] have synthesized octacene and nonacene. Motivated by their work, we have performed large-scale calculations of linear optical absorption of octacene and nonacene. Methodology adopted in our work is based upon Pariser-Parr-Pople model (PPP) Hamiltonian, along with large-scale multi-reference singles-doubles configuration interaction (MRSDCI) approach.

1. Introduction

Polyacenes are linear fused benzene rings known for their well-defined structures and crystalline forms [1-2]. Their applications in novel opto-electronic devices such as light-emitting field effect transistors make them experimentally and theoretically very important [3-5]. As compared to smaller acenes, the electronic structure and excited state properties of heptacene, octacene and larger acenes have not been fully explored because of increasing reactivity along the conjugation length [5-6]. Payne et al. [7] have synthesized heptacene single crystals. Octacene and nonacene have been synthesized by Tönshoff and Bettinger by using cryogenic matrix-isolation technique and a protection group strategy [8]. Although pentacene has often been reported to be the best available organic p-type semiconductor, larger acenes could be even more useful [9] for material applications [10-11].

In this paper we present the singlet linear optical absorption calculations of octacene and nonacene and compare the results with the experimental spectra [8].

2. Theory

The schematic structures of octacene and nonacene are shown in Figure 1. The molecule is assumed to lie in the *xy* -plane with the conjugation direction taken to be along the *x*-axis. The carbon-carbon bond length has been fixed at 1.4 Å, and all bond angles have been taken to be 120°. The reason of choosing this symmetric geometry, against various other possibilities has already been discussed in our earlier paper [21]. It can be noted that these structures can also be seen as two polyene chains of suitable lengths, coupled together along the *y*-direction.

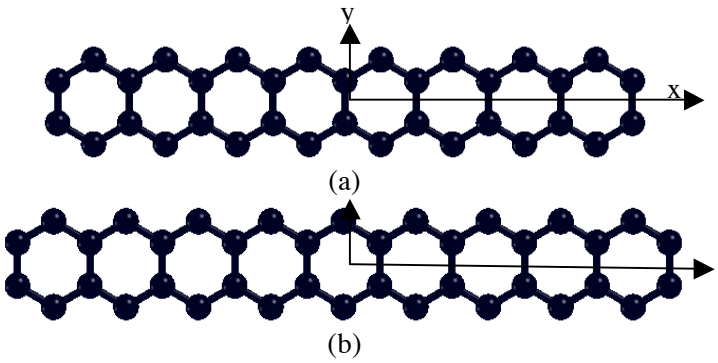

Figure 1. (a) Octacene and (b) Nonacene.

The correlated calculations are performed using the PPP model Hamiltonian [14], which can be written as

$$H = \sum_{i,j,\sigma} -t\ (c^{+}_{i\sigma}c_{j\sigma} + c^{+}_{j\sigma}c_{i\sigma}) + U\sum_{i} n_{i_\uparrow} n_{i_\downarrow} + \sum_{i<j} V_{i,j}(n_i - 1)(n_j - 1) \quad (1)$$

t = 2.4 eV is nearest neighbour hopping; U and $V_{i,j}$ are on site and long-range Coulomb interactions respectively.

The Coulomb interactions are parameterized according to the Ohno relationship [16]

$$V_{i,j} = \frac{1}{\kappa_{i,j}\sqrt{(1 + 0.6117R^2_{i,j})}} \quad (2)$$

$\kappa_{i,j}$ depicts the dielectric constant of the system which can simulate the effects of screening and R_{ij} is the distance in Å between i^{th} and the j^{th} carbon atoms. We have performed calculations using the "standard parameters (std. par.)" with U = 11.13 eV and $\kappa_{i,j}$ = 1 as well as the "screened parameters (scr. par.)" with U = 8 eV and $\kappa_{i,j}$ = 2 ($i \neq j$) and $\kappa_{i,i}$ = 1 [15].

The starting point of the correlated calculations for the molecules is the Restricted Hartree-Fock (RHF) calculations, using the PPP Hamiltonian. All the resultant HF molecular orbitals are treated as active orbitals. The many-body effects beyond RHF are computed using the Multi-Reference Singles Doubles Configuration Interaction (MRSDCI) method [17-20] in the following manner. After RHF calculations of the ground state 1^1A_g are performed, the MRSDCI calculation of the ground state, 1^1A_g and excited states, $^1B_{2u}$ and $^1B_{3u}$ by taking the lowest energy configuration of the D_{2h} symmetry (1^1B_{2u} is H→L and 1^1B_{3u} is H→L+1 and H-1→L where H and L corresponds to Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO)). From the CI calculations, we obtain the eigenfunctions and eigenvalues corresponding to the correlated ground and excited states of the examined molecules. Using these eigenfunctions the dipole matrix elements between the ground state and various excited states are computed. These dipole matrix elements, along with the energies of the excited states are, in turn, utilized to calculate linear optical absorption spectra. The above process is repeated with the MRSDCI calculations of ground and excited states with different references added to the previous ones based on a coefficient value, say (0.1 or more) and also the references corresponding to the important states in the previous optical spectra. This procedure is repeated until satisfactory convergence is achieved. Using the PPP model, the MRSDCI calculations of linear optical absorption of smaller acenes from naphthalene up to heptacene have already been performed in our group and it was shown that the screened parameter results are in better agreement with experimental results [21-22].

3. Results and Discussion

In this section we present the calculations on the optical absorption of octacene and nonacene from their lowest-singlet state (1^1A_g), and compare the results with the experimental ones.

3.1. Singlet Linear Optical Absorption Calculations

Here, we present the linear optical absorption spectra of octacene and nonacene computed using the standard (std.) and the screened (scr.) parameters in Figure 2 and Figure 3.

Tables 2-5 in the Appendix displays the detailed results of our theoretical singlet linear optical absorption calculations of octacene and nonacene, for the most important low-lying odd parity states of B_{2u} (*y*-polarized) and B_{3u} (*x*-polarized) states with respect to the ground state ($1^1A_g^-$) using both the parameters.

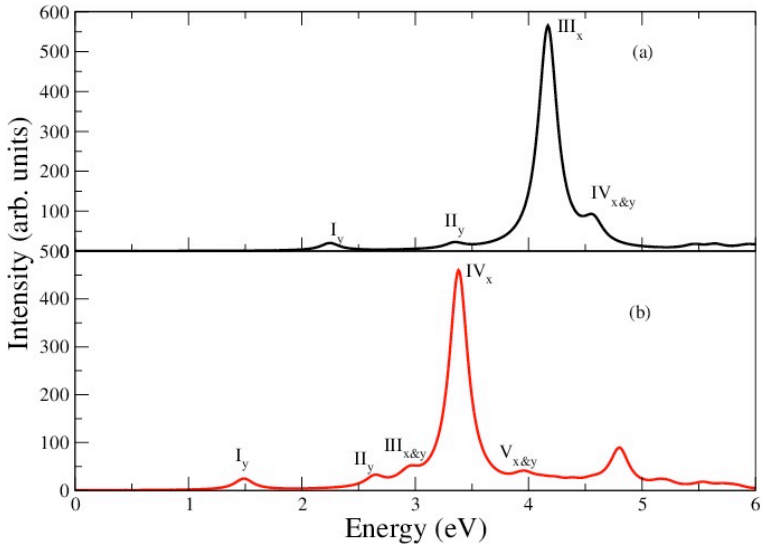

Figure 2. (color online) Linear optical absorption spectra of octacene using the (a) standard (black) and (b) screened (red) parameters. A uniform line width of 0.1 eV was assumed while plotting the spectra. The subscripts attached to the peak labels indicate the polarization directions *x* and *y*.

The singlet linear optical absorption of octacene and nonacene contains following features:

- Most of the intensity is concentrated in the *x*-polarized (long-axis polarized) spectra to the absorption into the $^1B_{3u}^+$ type of states, while the *y*-polarized (short-axis polarized) absorption into the $^1B_{2u}^+$ type states is very faint.
- The first peak is a weak peak, corresponds to the *y*-polarized, $1^1B_{2u}^+$ excited state of the system. The most important configuration contributing to the many-particle wave function of the state corresponds to $|H\rightarrow L\rangle$ excitation irrespective of the choice of the parameters.
- The second peak is a weak peak, corresponds to the *y*-polarized, $2^1B_{2u}^+$ excited state of the system. The most important configuration contributing to the many-particle wave function of the state corresponds to $|H\text{-}1\rightarrow L\text{+}1\rangle$ excitation irrespective of the choice of the parameters.
- The third peak corresponds to the *x*-polarized, $1^1B_{3u}^+$ excited state of the system and is the most intense state for the standard parameter case, whereas for the screened parameter results, it is a faint peak containing mixture of *x* and *y* polarized states, $1^1B_{3u}^+$ and $3^1B_{2u}^+$. The most important configuration contributing to the many-particle wave function for the standard parameter case, of the $1^1B_{3u}^+$ state, corresponds to $|H\rightarrow L\text{+}3\rangle$ and its charge conjugate, $|H\text{-}3\rightarrow L\rangle$ of octacene and $|H\text{-}4\rightarrow L\rangle$ and its charge conjugate, $|H\rightarrow L\text{+}4\rangle$ of nonacene, while that for the screened parameter case, of the $1^1B_{3u}^+$ state, is $|H\rightarrow L;\ H\text{-}1\rightarrow L\rangle$ and its charge

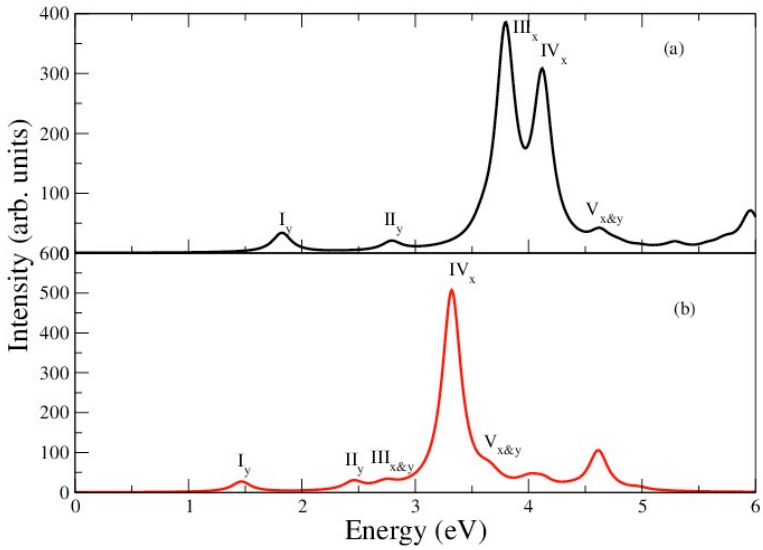

Figure 3. (color online) Linear optical absorption spectra of nonacene using (a) standard (black) and (b) screened (red) parameters. The rest of the information is same as in the caption of Figure 2.

conjugate $|H\rightarrow L; H\rightarrow L+1\rangle$, and of the $3^1B_{2u}^+$ state, is $|H\text{-}2\rightarrow L\rangle$ and its charge conjugate $|H\rightarrow L+2\rangle$ excitations for both octacene and nonacene.

- The fourth peak corresponds to the *x*-polarized, $2^1B_{3u}^+$ excited state of the system which is the most intense state of the system for the screened parameter case whereas for the standard parameter results, for octacene, it is a faint peak containing mixture of *x* and *y* polarized states, $2^1B_{3u}^+$ and $4^1B_{2u}^+$ while for nonacene, it corresponds to the *x*-polarized state, $2^1B_{3u}^+$ which is a higher intense state than that of octacene because of the splitting of the most intense state $1^1B_{3u}^+$ for the standard parameter case in nonacene, it has the same features as the most intense state. The most important configuration contributing to the many-particle wave function for the screened parameter case, of the $2^1B_{3u}^+$ state, is $|H\text{-}4\rightarrow L\rangle$ and its charge conjugate, $|H\rightarrow L+4\rangle$ for both octacene and nonacene, while that for the standard parameter case of octacene, for the $2^1B_{3u}^+$ state, is $|H\rightarrow L; H\text{-}1\rightarrow L\rangle$ and its charge conjugate $|H\rightarrow L; H\rightarrow L+1\rangle$ and of the $4^1B_{2u}^+$ state, is $|H\text{-}2\rightarrow L+2\rangle$ whereas that for nonacene for the $2^1B_{3u}^+$ state, is same as the most intense state, $|H\rightarrow L+4\rangle$ and its charge conjugate, $|H\text{-}4\rightarrow L\rangle$.
  In general, the most important configuration contributing to the many-particle wave function of the most intense state for the standard parameter case, for n = even oligomers e.g. octacene (n=8), are excitations $|H\rightarrow L+(n/2\text{-}1)\rangle$ and its charge conjugate, $|H\text{-}(n/2\text{-}1)\rightarrow L\rangle$, and for n= odd (n=9) e.g. nonacene, the excitations $|H\rightarrow L+(n\text{-}1)/2\rangle$ and its charge conjugate, $|H\text{-}(n\text{-}1)/2)\rightarrow L\rangle$ while for the screened parameter case, for n = even oligomers e.g. octacene, are excitations $|H\rightarrow L+n/2\rangle$ and its charge conjugate, $|H\text{-}n/2\rightarrow L\rangle$, and for n= odd e.g. nonacene, the excitations $|H\rightarrow L+(n\text{-}1)/2\rangle$ and its charge conjugate, $|H\text{-}(n\text{-}1)/2)\rightarrow L\rangle$.
- Another important state, namely $1^1B_{3u}^-$ state exists for all oligomers. Because it has the same particle-hole symmetry (-) as the ground state, in PPP calculations it does not contribute to the absorption spectrum. But many experiments report this state as a very weak feature in the absorption spectrum. It is at higher excitation energy than the $1^1B_{2u}^+$ state. The important configurations contributing to the wave function of this state are the doubly excited configurations, $|H\rightarrow L; H\text{-}1\rightarrow L\rangle$ which contribute significantly to this state. Thus, it is the electron-correlation effects which are responsible for its distinct location in the spectrum as compared to the $1^1B_{3u}^+$ state.

3.2. Comparison of Singlet Linear Optical Absorption with Experimental Absorption

We present comparison of the energies (eV) of most intense state of our singlet linear optical absorption with that of the experimental absorption spectra [8] of octacene and nonacene in Table 1. Hence, on the basis of the energies of the most intense state in the optical absorption spectra of octacene and nonacene, it is clear that our results match qualitatively with the experimental spectra irrespective of the parameters used. Quantitatively, our standard parameters results overshoot the excitation energies as compared to the experiments whereas the results based on the screened parameters show an opposite trend. This trend is reasonable as the standard parameters used to overestimate the gaps in general, so the screened parameters [15] were designed to include solid state or solvation effects (inter-chain screening). Therefore, our standard parameter results predict higher excitation energies as compared to the experiment and the same has been shown earlier in our group [21-22] for optical absorption of the lower acenes i.e. naphthalene up to heptacene. It has also been shown that the screened parameters agree well with experiments and other theoretical works as compared to the standard parameters. So, in our results, the screened parameters show lower energies with respect to experiments.

Further work on detailed comparison of our results with the experimental spectra and triplet excited state absorption calculations of octacene, nonacene and decacene is in progress [23].

The errors in terms of electron correlation (MRSDCI) and Hamiltonian (PPP model) are discussed below:

- MRSDCI approximation method is used for determination of the excitation energies of low-lying excited states which relies on an assumed cancellation of errors and thereby accurate prediction of the spectra [16-19]. As it is a variational method and any truncated CI has lesser no. of configurations than the full CI, so, energies predicted by them will be higher than those by full CI and hence, underestimates the correlations in ground and excited states. But the left out configurations in the MRSDCI method of both the ground and excited states will largely cancel out in the optical absorption calculations. Therefore, it gives a good description of the excitation state energies with respect to the ground state.
- In PPP model, only π electrons are considered explicitly, while the effect of σ-electrons are included in an implicit manner in terms of various parameters. Moreover, long range electron-electron interactions of density–density type are taken into account by means of suitable Coulomb parameters [12] while the rest are ignored. However, in spite of so many approximations involved, PPP model based calculations are extremely successful in describing the electronic structure of planar hydrocarbons in general, and their optical properties, in particular [13].

Table 1. Comparison of the energies of the most intense state of the absorption spectra of the theoretical and the experimental [8] work.

	Octacene		Nonacene	
Expt.	3.78		3.66	
	std. par.	scr. par.	std. par.	scr. par.
Theory	4.17	3.38	3.80	3.32

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Appendix

Table 2. Excited states contributing to the linear absorption spectrum of octacene computed using MRSDCI method coupled with the standard parameters in the PPP model Hamiltonian. The table includes many particle wave functions, excitation energies, and dipole matrix elements of various states with respect to the ground state. DF corresponds to the dipole forbidden state. Below, '+c.c.' indicates that the coefficient of charge conjugate of a given configuration has the same sign, while '-c.c.' implies that the two coefficients have opposite signs.

Peak	State	E(eV)	Transition Dipole (°A)	Wave Functions
DF	$1^1B_{3u}^-$	2.31	0	$\|H\rightarrow L;H-1\rightarrow L\rangle$-c.c.(0.4948)
I	$1^1B_{2u}^+$	2.24	0.905	$\|H\rightarrow L\rangle$(-0.8471)
II	$2^1B_{2u}^+$	3.34	0.641	$\|H-1\rightarrow L+1\rangle$(-0.5826)
III	$1^1B_{3u}^+$	4.17	3.622	$\|H\rightarrow L+3\rangle$+c.c.(0.4622)
IV	$2^1B_{3u}^+$	4.57	1.079	$\|H\rightarrow L;H\rightarrow L+1\rangle$+c.c.(0.3214)
	$4^1B_{2u}^+$	4.51	0.367	$\|H-2\rightarrow L+2\rangle$(-0.4148)

Table 3. Excited states contributing to the linear absorption spectrum of octacene computed using MRSDCI method coupled with the screened parameters in the PPP model Hamiltonian. The table includes many particle wave functions, excitation energies, and dipole matrix elements of various states with respect to the ground state. DF corresponds to the dipole forbidden state. Below, '+c.c.' indicates that the coefficient of charge conjugate of a given configuration has the same sign, while '-c.c.' implies that the two coefficients have opposite signs.

Peak	State	E(eV)	Transition Dipole (°A)	Wave Functions
DF	$1^1B_{3u}^-$	1.59	0	$\|H\rightarrow L;H-1\rightarrow L\rangle$–c.c.(0.5078)
I	$1^1B_{2u}^+$	1.49	1.241	$\|H\rightarrow L\rangle$(0.8503)
II	$2^1B_{2u}^+$	2.65	0.897	$\|H-1\rightarrow L+1\rangle$(-0.7244)
III	$1^1B_{3u}^+$	2.97	0.845	$\|H\rightarrow L;H-1\rightarrow L\rangle$-c.c.(0.4942)
	$3^1B_{2u}^+$	2.87	0.440	$\|H\rightarrow L+2\rangle$+c.c.(0.2638)
IV	$2^1B_{3u}^+$	3.38	3.675	$\|H-4\rightarrow L\rangle$+c.c.(0.5831)
V	$4^1B_{2u}^+$	3.97	0.641	$\|H-2\rightarrow L+2\rangle$(-0.5280)
	$3^1B_{3u}^+$	3.91	0.410	$\|H-2\rightarrow L;\ H-1\rightarrow L\rangle$-c.c.(0.4028)

Table 4. Excited states contributing to the linear absorption spectrum of nonacene computed using MRSDCI method coupled with the standard parameters in the PPP model Hamiltonian. The table includes many particle wave functions, excitation energies, and dipole matrix elements of various states with respect to the ground state. DF corresponds to the dipole forbidden state. Below, '+c.c.' indicates that the coefficient of charge conjugate of a given configuration has the same sign, while '-c.c.' implies that the two coefficients have opposite signs.

Peak	State	E(eV)	Transition Dipole (°A)	Wave Functions
DF	$1^1B_{3u}^-$	1.86	0	$\|H\rightarrow L;H\text{-}1\rightarrow L\rangle$+c.c.(0.4872)
I	$1^1B_{2u}^+$	1.82	1.328	$\|H\rightarrow L\rangle$(+0.8290)
II	$2^1B_{2u}^+$	2.79	0.733	$\|H\text{-}1\rightarrow L+1\rangle$(+0.5506)
III	$1^1B_{3u}^+$	3.80	3.037	$\|H\text{-}4\rightarrow L\rangle$-c.c.(0.3757)
IV	$2^1B_{3u}^+$	4.12	2.583	$\|H\rightarrow L+4\rangle$-c.c.(0.3943)
V	$3^1B_{3u}^+$	4.63	0.549	$\|H\rightarrow L+1;H\text{-}1\rightarrow L+1\rangle$-c.c.(0.3339)
	$5^1B_{2u}^+$	4.62	0.439	$\|H\rightarrow L;H\rightarrow L;\ H\text{-}1\rightarrow L+1\ \rangle$(+0.6215)

Table 5. Excited states contributing to the linear absorption spectrum of nonacene computed using MRSDCI method coupled with the screened parameters in the PPP model Hamiltonian. The table includes many particle wave functions, excitation energies, and dipole matrix elements of various states with respect to the ground state. DF corresponds to the dipole forbidden state. Below, '+c.c.' indicates that the coefficient of charge conjugate of a given configuration has the same sign, while '-c.c.' implies that the two coefficients have opposite signs.

Peak	State	E(eV)	Transition Dipole (°A)	Wave Functions
DF	$1^1B_{3u}^-$	1.51	0	$\|H\rightarrow L;H\rightarrow L+1\rangle$+c.c.(0.5143)
I	$1^1B_{2u}^+$	1.46	1.316	$\|H\rightarrow L\rangle$(0.8551)
II	$2^1B_{2u}^+$	2.45	0.935	$\|H\text{-}1\rightarrow L+1\rangle$(0.7260)
III	$3^1B_{2u}^+$	2.77	0.507	$\|H\rightarrow L+2\rangle$-c.c.(0.5434)
	$1^1B_{3u}^+$	2.75	0.611	$\|H\rightarrow L;\ H\rightarrow L+1\ \rangle$-c.c.(0.4901)
IV	$2^1B_{3u}^+$	3.32	3.887	$\|H\text{-}4\rightarrow L\rangle$-c.c.(0.5689)
V	$4^1B_{2u}^+$	3.70	0.559	$\|H\text{-}2\rightarrow L+2\rangle$(-0.4715)
	$3^1B_{3u}^+$	3.64	0.782	$\|H\text{-}2\rightarrow L;\ H\text{-}1\rightarrow L\rangle$+c.c.(0.3441)

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