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A correlated study of linear optical absorption in tetracene and pentacene

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Abstract

In this paper, we report large-scale configuration interaction (CI) calculations of linear optical absorption spectra of tetracene and pentacene. For the purpose, we used Pariser–Parr–Pople (P–P–P) model Hamiltonian and quadruple-CI (QCI) and multi-reference single–double CI (MRSDCI) approaches. The role of Coulomb parameters used in P–P–P Hamiltonian was also examined by considering standard parameters as well as screened set of parameters. Results are presented both for the long- and the short-axis-polarized components of the spectra and wave functions of various excited states have also been analysed.

1. Introduction

In recent years, oligoacenes have been considered to be leading candidates for novel opto-electronic devices, such as light emitting field effect transistors [1] and thin film transistors [2]. These materials crystallize nicely in well-defined structures; therefore, in oriented studies, they are preferable to conventional polymers like poly-*para*-phenylene (PPP) and poly-*para*-phenylene vinylene (PPV). In recent times, several authors have experimentally studied the optical properties of oligoacenes [3–8]. Moreover, some authors have also undertaken the theoretical studies of low lying excited states of oligoacenes [9–11]. However, to the best of our knowledge, so far, no theoretical calculations of linear absorption spectra of these materials have been reported. Therefore, in this work, we have performed large-scale correlated calculations of linear absorption spectra of tetracene and pentacene using Pariser–Parr–Pople (P–P–P) model Hamiltonian and CI method. Results are presented both for the long-axis-polarized and the short-axis-polarized components of the spectra and wavefunctions of various excited states have also been analysed. Additionally, the role of Coulomb parameters used in the P–P–P Hamiltonian has also been examined.

2. Theory

In this paper, we will adopt the notation ACENE-*n* to denote an acene oligomer containing '*n*' ($n = 4$ and 5) unit cells of benzene. The oligomers of ACENE-4 (tetracene) and ACENE-5 (pentacene) are shown in Fig. 1. Oligoacenes can be seen as benzene ring fused together or alternatively, as two parallel *trans*-polyacetylene chains coupled together by hopping and Coulomb interaction.

The correlated calculations on the oligoacenes were performed using the P–P–P model Hamiltonian, which can be written as,

$$H = H_{c_1} + H_{c_2} + H_{c_1 c_2} + H_{ee},$$

where H_{c_1} and H_{c_2} are the one-electron Hamiltonians for the carbon atoms located on first and second *trans*-polyacetylene (chain) respectively, $H_{c_1 c_2}$ the one-electron hopping between the two *trans*-polyacetylene chains and H_{ee} depicts the electron–electron repulsion. The individual terms can now be written as:

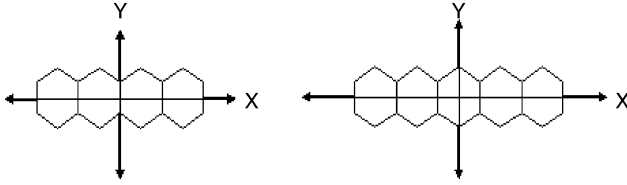$$H_{c_1} = -t_0 \sum_{\langle k, k' \rangle} B_{k, k'};$$

Fig. 1. Tetracene and pentacene.

$$H_{c_2} = -t_0 \sum_{\langle \mu, \nu \rangle} B_{\mu, \nu};$$

$$H_{c_1 c_2} = -t_\perp \sum_{\langle k, \mu \rangle} B_{k, \mu};$$

$$H_{ee} = U \sum_i n_{i\uparrow} n_{i\downarrow} + \frac{1}{2} \sum_{i \neq j} V_{i,j} (n_i - 1)(n_j - 1)$$

In the equation above, k, k' are carbon atoms on the first polyene chain, μ, ν are carbon atoms located on the second polyene chain, while i and j represent all the atoms of the oligomer and $B_{i,j} = \sum_\sigma (c_{i,\sigma}^+ c_{j,\sigma} + \text{h.c.})$. Matrix elements $t_0 = t_\perp = 2.4$ eV, depict one-electron hops. The Coulomb interactions are parameterized according to the Ohno relationsip [12]:

$$V_{i,j} = \frac{U}{\kappa_{i,j}} (1 + 0.6117 R_{i,j}^2)^{1/2},$$

where $\kappa_{i,j}$ depicts the dielectric constant of the system, which can simulate the effects of screening, U the on-site repulsion term and $R_{i,j}$ is the distance in angstroms between the ith carbon and the jth carbon. In the present work, we have tried two parameter sets: (a) "standard parameters" with $U = 11.13$ eV and $\kappa_{i,j} = 1.0$ and (b) "screened parameters" of Chandross and Mazumdar [13] with $U = 8.0$ eV and $\kappa_{i,j} = 2.0$ for $i \neq j$ and $\kappa_{i,j} = 1.0$ for $i = j$.

The starting point of the correlated calculations for various oligomers were the restricted Hartree–Fock (HF) calculations, using the PPP Hamiltonian. The many-body effects beyond HF were computed using different levels of CI methods, namely quadruple-CI (QCI) and multi-reference singles–doubles CI (MRSDCI). Details of these CI-based many-body procedures have been presented in our earlier works [14,15]. We use full D_{2h} symmetry of oligomers in our calculations. In our notations, an x-polarized photon excites the system from ground state ($1A_g$) to B_{1u} states and y-polarized photon excites the system from ground state to B_{2u} states.

3. Calculations and results

In this section, first we will briefly present linear absorption spectra obtained from tight-binding Hamiltonian and next, we will discuss in details the main features of linear optical spectra of tetracene and pentacene obtained using the P–P–P Hamiltonian.

3.1. Hückel model calculations

The one-electron model calculations were performed using tight-binding Hückel model Hamiltonian and the calculated spectra of ACENE-2, ACENE-5, ACENE-10 and ACENE-20 are presented in Fig. 2. From Hückel model Hamiltonian, as expected the obtained first peak corresponds to $H \rightarrow L$ transition, while the highest intensity peak is x-polarized. As the value of n increases in ACENE-n, the intensity of the first y-polarized peak decreases while the intensity of first x-polarized peak increases and off course, the spectrum is
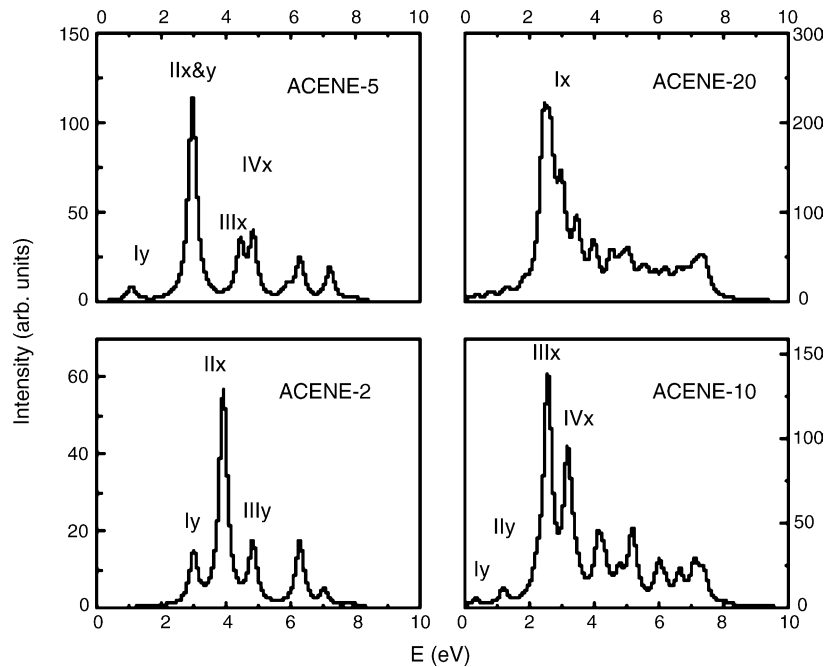

Fig. 2. Spectrums of ACENE-2, 5, 10 and 20 using one-electron Hückel model Hamiltonian.

Table 1
Comparision of different results

	n			
	2	3	4	5
Standard parameters[a]				
$E(1B_{1u})$	3.61	3.25	3.36	3.42
$E(1B_{2u})$	4.45	3.66	3.16	2.86
Screened parameters[a]				
$E(1B_{1u})$	3.22	2.91	3.28	3.47
$E(1B_{2u})$	4.51	3.55	2.97	2.65
Hummer et al.				
$E(1B_{1u})$	5.6	5.1	4.5	3.9
$E(1B_{2u})$	4.8	3.7	2.7	1.9
Tavan et al.				
$E(1B_{1u})$	5.63	4.68	4.22	3.7
$E(1B_{2u})$	5.68	3.27	2.62	2.89
Raghu et al.[b]				
$E(1B_{2u})$	–	3.68	3.20	2.92
Experimental				
E	4.34[c]	3.31[d]	3.43[g]	2.83[g]
	–	4.40[e]	2.67[c]	2.28[h] (1B$_{1u}$)
	–	4.15[f]	–	
	–	3.35[c]	–	3.66[h] (1B$_{2u}$)
	–	–	–	2.11[c]

[a] Our work.
[b] Ref. [10].
[c] Ref. [8].
[d] Ref. [6].
[e] Ref. [3].
[f] Ref. [5].
[g] Ref. [4].
[h] Ref. [7].

red shifted. The decrease in $H \rightarrow L$ intensity is understandable because for the present choice of tight-binding parameters, the system is metallic in the thermodynamic limit. For oligomers with even value of 'n', the highest intensity x-polarized peak corresponds to $H \rightarrow L + n/2$ transition, while with odd values of 'n', it corresponds to $H \rightarrow L + (n + 1)/2$ transition. Thus, we conclude that in the tight-binding model for $n \rightarrow \infty$, the peak is x-polarized and carries most of the intensity. For example, we can see the spectrum of ACENE-20 presented in Fig. 2, in which x-polarized peak carries most of the intensity.

3.2. P–P–P model calculations

Now, we present the results of our correlated calculations of linear absorption on oligoacenes performed using P–P–P model Hamiltonian and two sets of Coulomb parameters, mentioned earlier. For the purpose of comparison with other author's results, we performed excited state calculations on oligomers from ACENE-2 to ACENE-5. Excitation energies obtained from those calculations along with the theoretical results of other authors, as well as experimental results are presented in Table 1. Additionally, calculated spectra using screened parameters for ACENE-4 and ACENE-5 are also presented in Fig. 3. The correlated calculations for ACENE-4 and ACENE-5 were performed

Table 2
Details of number of reference states (N_{ref}) and the size of the Hamiltonian matrix (N_{total}) for various symmetry manifolds of ACENE-4 and ACENE-5

State	Method	ACENE-4		ACENE-5	
		N_{ref}	N_{total}	N_{ref}	N_{total}
A$_g$	QCI	1	193538	1	1002597
B$_{1u}$	MRSDCI	42	50450	34	126690
B$_{2u}$	QCI	1	335325	1	1707243

using QCI methodology for B$_{2u}$ states and MRSDCI methodology for B$_{1u}$ states. These correlated calculations presented here were very large-scale and details related to their size are presented in Table 2. Recently, the most extensive calculations of low lying excited states of polyacenes were carried out by Raghu et al [10] using the DMRG method and they confined their calculations to B$_{2u}$ states. Inspection of Table 1 reveals that our results obtained using standard parameters for B$_{2u}$ states are in very good agreement with results obtained by Ramasesha et al. Experimental results are also in good agreement with our results, obtained using screened parameters.

Experimentalists classify the absorption spectra of oligoacene broadly in three bands, namely p, α and β bands [16]. The p-band of polyacenes is identified as a $\pi–\pi^*$ transition described by mainly $H \rightarrow L$ (HOMO $\rightarrow$ LUMO) transitions. The α- and β-bands are identified as $\pi–\pi^*$ transition described by mainly $H - 2 \rightarrow L$ or $H \rightarrow L + 2$ transitions [17]. Next, we analyse the theoretical spectra presented in Fig. 3. We observe that in tetracene first peak corresponds to x-polarized transition denoting 1B$_{1u}$ excited state while in pentacene, the first peak corresponds to a y-polarized transition leading to 1B$_{2u}$ state. For ACENE-4, although the energy of 1B$_{1u}$ state is very close to that of 1B$_{2u}$ state, 1B$_{2u}$ state has negligible dipole coupling to the ground state. Thus, our prediction is that in oriented samples of tetracene, the first optical absorption is x-polarized. This is unlike the case of pentacene for which the first optical peak indeed corresponds to the 1B$_{1u}$ state, composed mainly of $H \rightarrow L$ excitation.

Another remarkable fact about ACENE-4 absorption spectra is that as compared to the tight-binding results the intensity of x-polarized peaks has been distributed over three excited states—1B$_{1u}$, 2B$_{1u}$ and 3B$_{1u}$, out of which two of them are predominantly composed of $|H \rightarrow L + 2 > + c.c.$ one-electron excitation (see Table 3). The first y-polarized peak of ACENE-4 is

Table 3
Excited states in tetracene using screened parameters

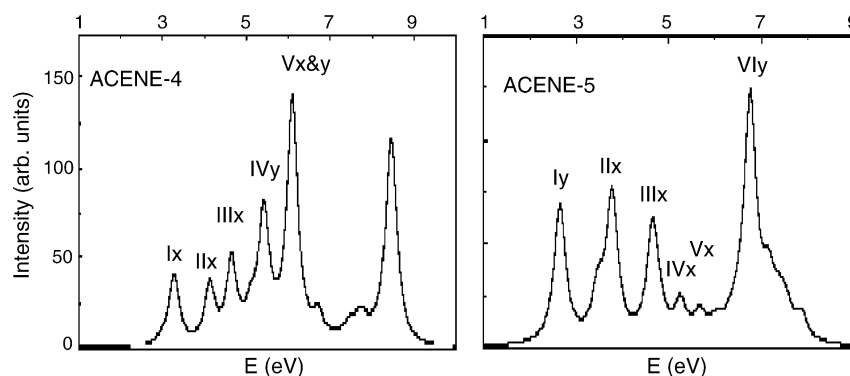| Peak	State	Energy (eV)	Wave function
I	1B$_{1u}$	3.28	$|H \rightarrow L + 2 > + c.c.$ (0.57)
II	2B$_{1u}$	4.13	$|H \rightarrow L; H - 1 \rightarrow L > + c.c.$ (0.49)
III	3B$_{1u}$	4.65	$|H \rightarrow L + 2 > + c.c.$ (0.62)
IV	3B$_{2u}$	5.41	$|H - 1 \rightarrow L + 1 >$ (0.77)
			$|H \rightarrow L + 3 > + c.c.$ (0.21)
V	7B$_{1u}$ and 4B$_{2u}$	6.10	$|H \rightarrow L; H \rightarrow L + 1 > + c.c.$ (0.50)
			$|H - 1 \rightarrow L + 4 > + c.c.$ (0.21)
			$|H - 2 \rightarrow L + 2 >$ (0.80)

Fig. 3. Spectrums of ACENE-4 and 5 using P–P–P model Hamiltonian using screened parameters.

Table 4
Excited states in pentacene using screened parameters

Peak	State	Energy (eV)	Wave function
I	$1B_{2u}$	2.65	$|H \to L> (0.85)$
II	$2B_{1u}$	3.78	$|H \to L; H \to L+1> + c.c. (0.46)$
			$|H \to L+2> + c.c. (0.25)$
III	$3B_{1u}$	4.65	$|H \to L+2> + c.c. (0.26)$
IV	$5B_{1u}$	5.24	$|H \to L; H \to L+5> + c.c. (0.26)$
			$|H \to L; H-1 \to L+3> + c.c. (0.25)$
			$|H \to L+1; H \to L+3> + c.c. (0.21)$
V	$8B_{1u}$	5.67	$|H \to L+7> + c.c. (0.32)$
			$|H \to L+1; H-1 \to +1> + c.c. (0.21)$
VI	$11B_{2u}$	6.77	$|H-3 \to L+3> + c.c. (0.75)$

predicted to be at rather high energy of 5.41 eV and consists mainly of $|H-1 \to L+1>$ transition.

Although, in one-electron theory, $H \to L$ transition does not have very high intensity, but in correlated models, it has significant intensity for oligoacenes containing odd number of rings and even for oligoacenes with even number of rings, y-polarized transitions contribute sighnificantly to the intensity (not $H \to L$ but $H-1 \to L+1$).

As mentioned earlier that in pentacene the first peak corresponds to $|H \to L>$ while the second peak has slightly higher intensity and corresponds to x-polarized transition leading to $2B_{1u}$ state. This state is seen to be a strong mixture of double excitation and $|H \to L+2>$ single excitation (see Table 4).

This clearly indicates the influence of electron correlation effects. The x-polarized polarized transition which is predominantly $|H \to L+2>$, there is another x-polarized transition corresponding to $3B_{1u}$ state. Next, we would like to comment on some very high energy bands. These bands correspond to mainly single excitation involving orbitals away from the Fermi level. In Tables 3 and 4, we present the energies and wave functions of various excited states, which are visible in the linear absorption spectra of tetracene and pentacene respectively. It can be easily concluded from Fig. 3 and Table 1 that as the 'n' increases in ACENE-n, the spectrum gets red shifted. More detailed analysis of the linear spectra of oligoacenes will be presented elsewhere [18].

4. Conclusions

In conclusion, we have presented large-scale correlated calculations of linear optical absorption spectra of tetracene and pentacene. It has been shown that electron correlation effects have significant influence on calculated spectra. Moreover, using the results of our calculations we are in a position to predict the polarizations of various optical transitions in these materials, which could be verified in future experiments.

Acknowledgement

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