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Large Scale Configuration Interaction Calculations of Linear Optical Absorption of Decacene

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Abstract. The technological importance of higher acenes has led to resurgence of interest in synthesizing them e.g. octacene, nonacene and decacene [1]. Recently, Tönshoff and Bettinger have synthesized octacene and nonacene [2]. Motivated by their work, we have performed large scale calculations of linear optical absorption of decacene. 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.

Keywords: Decacene, Acenes; Linear Optical Absorption; Configuration Interaction
PACS: 78.30.Jw; 78.20.Bh; 42.65.-k

INTRODUCTION

Larger acenes have lot of technological importance [1] in opto-electronic applications. Recently efforts have been made to synthesize them. Using, low temperature matrix isolation techniques, Tönshoff and Bettinger have synthesized octacene and nonacene [2]. But decacene has not been synthesized as yet. Motivated by their work, we have performed linear optical absorption calculations of decacene. We hope that our results might generate interest to the experimentalists and other theoretical researchers to work on decacene and confirm the findings.

THEORY

The schematic structure of decacene is shown in Fig. 1. The molecule is assumed to lie in the *x-y* 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 [10]. It can be noted that these structures can also be seen as two polyene chains of suitable lengths, coupled together along the *y*–direction.

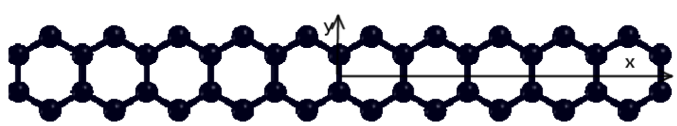

FIGURE 1. Decacene ($C_{42}H_{24}$)

The correlated calculations are performed using the PPP model Hamiltonian [3]

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

where t=2.4 eV is nearest-neighbor 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 [5]

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

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where, κ_{ij} 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 κ_{ij}=1 as well as the "screened parameters (scr. par.)" [4] with U=8 eV and κ_{ij}=2 ($i \neq j$) and κ_{ii}=1. Using the PPP model, linear optical absorption calculations of smaller acenes namely from naphthalene up to heptacene have already been performed in our group. It is reported that the screened parameter results are in better agreement with experimental work as compared to the results obtained using the standard parameter [10-11].

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 [6-9] in the following manner. After RHF calculations of the ground state $1A_g$ are performed, the MRSDCI calculation of the ground state, $1A_g$ and excited states, B_{2u} and B_{3u} by taking the lowest energy configuration of the D_{2h} symmetry ($1B_{2u}$ is H→L and $1B_{3u}$ 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.

RESULTS AND DISCUSSION

Singlet Linear Optical Absorption Calculations

Here, we present the results of our correlated calculations of singlet linear optical absorption spectra of decacene as shown in Fig. 2 using both the standard (std.) and screened (scr.) parameters. Table.1 shows the results of the three lowest odd parity states of y-polarized B_{2u} and x-polarized B_{3u} states with respect to the ground state $1A_g^-$ for both the parameters. The many body wave function analysis of the linear optical absorption spectrum of the decacene for std. and scr. parameters is presented in Table.2 and Table.3 respectively.

TABLE (1). Energies (eV) of three lowest states of the singlet linear absorption calculations of decacene mputed using the standard (std.) and the screened (scr.) parameters.

State	std. par.	scr. par.
$1B_{3u}^-$	1.72	1.15
$1B_{2u}^+$	1.79	1.27
$1B_{3u}^+$	3.68	2.42

The singlet linear optical absorption of decacene contains following features:

- The *x*-polarized spectra dominate the absorption spectra as the *y*-polarized spectra are very faint. The screened parameter spectra are red shifted as compared to the standard parameter ones.
- The first and second peaks correspond to the y-polarized, $1B_{2u}^+$ and $2B_{2u}^+$ excited states of the system respectively irrespective of the choice of the parameters. The most important configuration contributing to the many-particle wave function of $1B_{2u}^+$ and $2B_{2u}^+$ states corresponds to \|H→L> and \|H-1→L+1> excitation respectively. This feature of the first peak is similar to the results performed on smaller acenes namely naphthalene up to heptacene earlier in our group [10]. However, the second *y*-polarized peak is absent in the smaller acenes spectra.
- The third peak corresponds to the *x*-polarized, $1B_{3u}^+$ excited state of the system for the standard parameter case whereas it is a faint peak for the screened parameter case, containing mixture of *x* & *y* polarized states, $3B_{2u}^+$ and $1B_{3u}^+$. The most important configuration contributing to the many-particle wave function of the third peak for the standard parameter case corresponds to double excitations, \|H→L; H→L+1> and its charge conjugate \|H→L; H-1→L> while that for the screened parameter, double excitations, \|H→L; H→L+1> and its charge conjugate \|H→L; H-1→L> for the $1B_{3u}^+$ state and \|H-2→L> and its charge conjugate \|H→L+2> for the $3B_{2u}^+$ state.

- The fourth peak also corresponds to the *x*-polarized, $2B_{3u}^{+}$ excited state of the system and is the most intense state for the standard parameter case whereas for the screened parameter case it is comparatively weaker peak containing mixture of *x* & *y* polarized states, $4B_{2u}^{+}$ and $2B_{3u}^{+}$. The most important configuration contributing to the many-particle wave function of the fourth peak for the standard parameter is a single excitation |H→L+4> and its charge conjugate, |H-4→L> while that for the screened parameter is double excitation |H→L+1; H→L+2> and its charge conjugate |H-1→L; H-2→L> for the $4B_{2u}^{+}$ state and |H-2→L+2> for the $2B_{3u}^{+}$ state.
- The fifth peak is a faint peak containing mixture of *x* & *y* polarized states $5B_{2u}^{+}$ and $3B_{3u}^{+}$ for the standard parameter case while it is the most intense state for the screened parameter case, containing mixture of $5B_{2u}^{+}$ and $4B_{3u}^{+}$ states. The most important configuration contributing to the many-particle wave function of the fifth peak for the standard parameter case is a double excitation |H→L; H→L;H-1→L+1> for the $5B_{2u}^{+}$ state and a double excitation |H-1→L; H-1→L+1> and its charge conjugate |H→L+1; H-1→L+1> for the $3B_{3u}^{+}$ state, while that for the screened parameter case is a double excitation |H→L; H→L; H-1→L+1> for the $5B_{2u}^{+}$ state and a single excitation |H→L+5> and its charge conjugate |H-5→L> for the $4B_{3u}^{+}$ state.
- Another important state, namely $1B_{3u}^{-}$ 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 lower excitation energies than the $1B_{2u}^{+}$ state for decacene. However, this is opposite to the results of smaller acenes namely tetracene up to nonacene, where the $1B_{3u}^{-}$ state is at higher energies than the first allowed $1B_{2u}^{+}$ state. Therefore, surprisingly, this ordering of the state in decacene is in agreement with that in small acenes namely naphthalene and anthracene. The important configurations contributing to the wave function of this state are the doubly excited configurations 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 $1B_{3u}^{+}$ state.

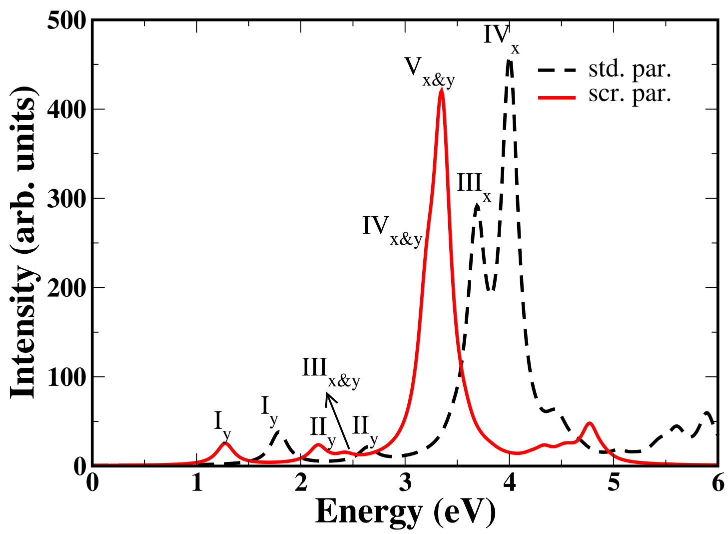

FIGURE 2. Linear optical absorption spectra of decacene using standard (dashed) and screened (solid) parameters.

TABLE (2). Excited states contributing to the linear absorption spectrum of decacene computed using the 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 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(Å)	Wavefunction
DF	$1B_{3u}^{-}$	1.72	0	$\vert H\rightarrow L; H\rightarrow L+1\rangle$ -c.c.(0.4790)
I	$1B_{2u}^{+}$	1.79	1.423	$\vert H\rightarrow L\rangle$ (-0.8203)
II	$2B_{2u}^{+}$	2.64	0.776	$\vert H-1\rightarrow L+1\rangle$ (-0.5607)
III	$1B_{3u}^{+}$	3.68	2.554	$\vert H\rightarrow L; H\rightarrow L+1\rangle$ +c.c.(0.3710)
IV	$2B_{3u}^{+}$	4.00	3.293	$\vert H-4\rightarrow L\rangle$ +c.c.(0.4451)
V	$3B_{3u}^{+}$	4.46	0.739	$\vert H-1\rightarrow L; H-1\rightarrow L+1\rangle$ +c.c.(0.3459)
	$5B_{2u}^{+}$	4.40	0.505	$\vert H\rightarrow L; H\rightarrow L; H-1\rightarrow L+1\rangle$ (-0.6203)

TABLE (3). Excited states contributing to the linear absorption spectrum of decacene computed using the 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 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(Å)	Wavefunction
DF	$1B_{3u}^{-}$	1.15	0	$\vert H\rightarrow L; H-1\rightarrow L\rangle$ -c.c.(0.4851)
I	$1B_{2u}^{+}$	1.27	1.369	$\vert H\rightarrow L\rangle$ (-0.8338)
II	$2B_{2u}^{+}$	2.16	0.929	$\vert H-1\rightarrow L+1\rangle$ (+0.7110)
III	$1B_{3u}^{+}$	2.42	0.295	$\vert H\rightarrow L; H\rightarrow L+1\rangle$ +c.c.(0.4762)
	$3B_{2u}^{+}$	2.42	0.417	$\vert H-2\rightarrow L\rangle$ +c.c.(0.5220)
IV	$2B_{3u}^{+}$	3.20	1.872	$\vert H\rightarrow L+1; H\rightarrow L+2\rangle$ +c.c.(0.3455)
	$4B_{2u}^{+}$	3.21	0.706	$\vert H-2\rightarrow L+2\rangle$ (-0.5140)
V	$4B_{3u}^{+}$	3.35	3.259	$\vert H\rightarrow L+5\rangle$ +c.c.(0.4970)
	$5B_{2u}^{+}$	3.35	0.464	$\vert H\rightarrow L; H\rightarrow L; H-1\rightarrow L+1\rangle$ (+0.6272)

CONCLUSION

In this paper, we presented a large scale correlated study of linear optical absorption and low-lying excited states of decacene. Some aspects of the linear optical spectrum of smaller acenes namely naphthalene up to heptacene [10] is found to be very similar to the decacene. For example, the first peak of the spectrum corresponds to $1B_{2u}^{+}$ state, and the most intense peak corresponds to a mixture of *x* and *y*-polarized states. However, there are some differences, the second *y*-polarized peak is absent in the smaller acenes spectrum and the first x-polarized state is the most intense state in the smaller acenes spectrum and the dipole forbidden $1B_{3u}^{-}$ state at higher excitation energies than the $1B_{2u}^{+}$ state for smaller acenes spectrum.

In this paper we restricted ourselves to the low-lying excited states of decacene which contribute to its linear optical properties. However, it will also be interesting to explore the nature of their two-photon states, which will contribute to the nonlinear, as well as excited-states absorption in these materials. Further work on linear singlet absorption states and triplet excited states of the higher acenes such as octacene, nonacene and decacene is in progress [12].

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REFERENCES

1. S.S. Zade and M. Bendikov, *Angew. Chem. Ed.* **122**, 4104-4107 (2010).
2. C. Tönshoff and H. F. Bettinger, *Angew. Chem. Int. Ed*. **49**, 4125-4128 (2010).
3. P. Sony and A. Shukla, *Comp. Phys. Comm.* **181(4)**, 821-830 (2010).
4. M. Chandross and S. Mazumdar, *Phys. Rev. B* **55**, 1497-1504 (2010).

5. K. Ohno, *Theor. Chim. Acta.* **2**, 219-227 (1964).
6. H. Ghosh, A. Shukla and S. Mazumdar, *Phys. Rev. B* **62**, 12763-12774 (2000).
7. Shukla, *Phys. Rev. B* **65**, 12504(1-2) (2002).
8. A. Shukla, *Chem. Phys.* **300**, 177-188 (2004).
9. A.Shukla, *Phys. Rev. B* **69**, 165218(1-10) (2004).
10. P. Sony and A. Shukla, *Phys. Rev. B* **75**, 155208(1-22) (2007).
11. P. Sony and A. Shukla, *J. Chem. Phys*. **131**, 014302(1-7) (2009).
12. H. Chakraborty and A. Shukla, under preparation.