Theory of Triplet Optical Absorption in Oligoacenes: From Naphthalene to Heptacene

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Abstract

In this paper we present a detailed theory of the triplet states of oligoacenes containing up to seven rings, i.e., starting from naphthalene all the way up to heptacene. In particular, we present results on the optical absorption from the first triplet excited state $1^3B_{2u}^+$ of these oligomers, computed using the Pariser-Parr-Pople (PPP) model Hamiltonian, and a correlated electron approach employing the configuration-interaction (CI) methodology at various levels. Excitation energies of various triplets states obtained by our calculations are in good agreement with the experimental results, where available. The computed triplet spectra of oligoacenes exhibits rich structure dominated by two absorption peaks of high intensities, which are well separated in energy, and are caused by photons polarized along the conjugation direction. This prediction of ours can be tested in future experiments performed on oriented samples of oligoacenes.

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I. INTRODUCTION

Conjugated polymers form a class of materials which are strong candidates for building the next generation of optoelectronic devices.\textsuperscript{1,2} In order to be able utilize them for these purposes, a thorough understanding of their electronic structure and optical properties is essential. Most of the polymers useful for optoelectronic devices have singlet ground states, and, therefore, singlet excited states determine their optical properties. As a result of that, most of the theoretical studies of optical properties of conjugated polymers, have concentrated on the absorption spectra in the singlet manifold.\textsuperscript{3} However, the triplet states of these systems have become important because of the possibility of “singlet fission”, i.e., a singlet excited state decaying into two triplets leading to higher photo voltaic yield.\textsuperscript{4,5} Furthermore, within the tight-binding model, the lowest triplet state has the same orbital occupancy and spatial symmetry as the lowest optically active singlet state, thus rendering them degenerate. Therefore, differences between these two states will be due to electron correlation effects, and, thus, a study of triplet states provides us with an insight into the role of electron correlations in that material.\textsuperscript{6}

Recently, polyacenes have been considered as strong candidates for optoelectronic device applications such as light-emitting diodes, and field effect transistors.\textsuperscript{7–10} Furthermore, because of their structural similarities to zigzag graphene nanoribbons,\textsuperscript{7,11} the research effort involving various oligoacenes has further intensified. Although, most of the studies have concentrated on oligoacenes ranging from naphthalene to pentacene, several recent works have reported the synthesis of longer oligomers such as hexacene, heptacene, and beyond.\textsuperscript{12–15} Over the years, optical properties of oligoacenes have been studied extensively, however, most of these studies have been confined to their ground state absorption into higher singlet states,\textsuperscript{7,8,16} with the number of studies dedicated to triplet states being far fewer. Triplet states of naphthalene have been probed experimentally by Lewis et al.,\textsuperscript{17} McClure,\textsuperscript{18} Hunziker,\textsuperscript{19,20} and Meyer et al.\textsuperscript{21} Similarly, experimental measurements of the triplet states in longer stable oligomers namely anthracene,\textsuperscript{21–24} tetracene,\textsuperscript{21–23,25–27} and pentacene,\textsuperscript{27–29} have also been performed. A few triplet state measurements of relatively unstable hexacene,\textsuperscript{30} and heptacene\textsuperscript{12} also exist. Recently, several experimental measurements of the triplet states have also been performed on thin films, crystalline, and dimeric samples of tetracene\textsuperscript{31,32} and pentacene,\textsuperscript{32–37} predicting that the lowest triplet state is of charge transfer type.
As far as theoretical studies of the triplet states of oligoacenes are concerned, using a Pariser-Parr-Pople (PPP) model type semi-empirical approach, early calculations were performed by Pariser. Subsequently, again using the PPP model, low-order configuration interaction (CI) calculations of triplet states of various oligoacenes were performed by Groot and Hoytink, and Angliker et al. A self-consistent-field random-phase-approximation (SCF-RPA) scheme also within the PPP model was employed by Baldo et al. to perform calculations of triplet states in polyacenes. Large scale density matrix renormalization group (DMRG) based calculations using the PPP model, have been performed by Ramasesha and co-workers, and recently, they reported exact diagonalization (full CI) calculations, for tetracene. Complete neglect of differential overlap (CNDO) based CI calculations employing CNDO/S2 parameterization were done by Lipari and Duke, while CNDO/2 parameters were used by Sanche and co-workers to perform triplet excited state calculations. Gao et al. employed a spin Hamiltonian and valence bond approach to compute the triplet states of oligoacenes. As far as \textit{ab initio} calculations are concerned, complete-active-space self-consistent field (CASSCF) and perturbation theory (PT2F) calculations on these systems were performed by Rubio et al., while multi-reference Møller-Plesset (MRMP) theory calculations were reported by Hirao and co-workers, and Zimmerman et al. Chan and co-workers reported calculations of triplet states of oligoacenes combining the CASSCF and density-matrix renormalization group (DMRG) approaches, while coupled-cluster theory (CCSD(T)) based calculations were performed by Hajgato et al. Numerous first-principles density-functional theory (DFT) based calculations have also been performed by various authors which include works of Houk et al., Quartì et al., Anger and co-workers, Hummer et al., Bendikov et al., Nguyen et al., and spin-polarized DFT calculations by Jiang and Dai. Most of the theoretical studies mentioned above either concentrated on a class of triplet excited states of small oligomers, or only on the energetics of their lowest triplet excited state. However, none of the earlier works have reported the calculations of triplet optical absorption spectra, which involves not only the energetics and the wave functions of a number of triplet excited states, but also computation of their transition dipole moments with respect to the lowest triplet state.

In this work, we have performed large-scale correlated electron calculations of optical absorption in the triplet manifolds of oligoacenes ranging from naphthalene up to heptacene, using the multi-reference singles-doubles CI (MRSDCI) method, employing the PPP model
Hamiltonian. The detailed results obtained for the low-lying triplet excited states of these acenes are presented and compared with different experimental and other theoretical works. Our calculated energies of the lowest triplet excited states, $1^3B_{2u}^+$, $1^3B_{1g}^-$, $1^3B_{1g}^+$, $1^3A_g^-$, and $1^3A_g^+$ for these oligoacenes show very good agreement with the experimental results. The calculated triplet absorption spectra of these oligoacenes reveal two long-axis polarized intense peaks which are well separated in energy, as against one intense peak observed in their singlet absorption spectra. This observation is in agreement with our earlier triplet absorption calculations of the longer acenes namely octacene, nonacene and decacene, and can be tested in future experiments on the oriented samples of oligoacenes.

Remainder of this paper is organized as follows. In the next section we describe the theoretical methodology employed for performing these calculations. Then, in section III, we present and discuss our results. Finally, in section IV, we present our concluding remarks, while the quantitative details of the excited states contributing to the absorption spectra, along with their many-particle wave functions are presented in the Appendix.

II. THEORY

The schematic structure of an oligoacene is shown in Fig.1, with the molecule assumed to be lying in the $xy$-plane, and the conjugation direction taken to be along the $x$-axis. These calculations have been performed assuming a highly symmetric geometry of oligoacenes, with all nearest neighbor carbon-carbon bond length fixed at 1.4 Å, and all the bond angles taken to be 120°. The reason behind choosing this symmetric geometry is computational simplicity. However, by means of explicit calculations, we recently demonstrated that the optical absorption results obtained using asymmetric geometries, with non-uniform bond lengths and bond angles, do not exhibit any significant differences as compared to the symmetric geometry adopted in the present work. We note that these symmetric structures can also be seen as two identical polyene chains of suitable lengths, separated from each other along the $y$-direction.
The correlated calculations are performed using the PPP model Hamiltonian,\textsuperscript{38,39} which can be written as

\begin{equation}
H = H_{C_1} + H_{C_2} + H_{C_1C_2} + H_{ee},
\end{equation}

where \( H_{C_1} \) and \( H_{C_2} \) are the one-electron Hamiltonians for the carbon atoms located on the upper and the lower polyene like chains, respectively. \( H_{C_1C_2} \) is the one-electron hopping between the two chains, and \( H_{ee} \) depicts the electron-electron repulsion. In the second-quantized notation, the individual terms can now be written as,

\begin{equation}
H_{C_1} = -t_0 \sum_{\langle k,k' \rangle} B_{k,k'},
\end{equation}

\begin{equation}
H_{C_2} = -t_0 \sum_{\langle \mu,\nu \rangle} B_{\mu,\nu},
\end{equation}

\begin{equation}
H_{C_1C_2} = -t_\perp \sum_{\langle k,\mu \rangle} B_{k,\mu},
\end{equation}

\begin{equation}
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)
\end{equation}

In the equation above, \( k, k' \) are carbon atoms on the upper polyene chain, \( \mu, \nu \) are carbon atoms located on the lower polyene chain, while \( i \) and \( j \) represent all the atoms of the oligomer. Symbol \( \langle \ldots \rangle \) implies nearest neighbors, and \( B_{i,j} = \sum_{\sigma} (c_{i,\sigma}^\dagger c_{j,\sigma} + h.c.) \), where h.c. denotes the Hermitian conjugate. Matrix elements \( t_0 \) and \( t_\perp \) depict one-electron hops. As far as the values of the hopping matrix elements are concerned, we took \( t_0 = 2.4 \text{ eV} \) for both
intracell and intercell hopping, and $t_\perp = t_0$ consistent with the undimerized ground state for polyacene argued by Raghu et al.\textsuperscript{43}

The Coulomb interactions are parametrized according to the Ohno relationship,\textsuperscript{60}

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

where, $\kappa_{i,j}$ depicts the dielectric constant of the system which can simulate the effects of screening, $U$ is the on-site repulsion term, and $R_{i,j}$ is the distance in Å between the $i$th carbon and the $j$th carbon. In the present work, we have performed calculations using “standard parameters”\textsuperscript{60} with $U = 11.13$ eV and $\kappa_{i,j} = 1.0$, as well as “screened parameters”\textsuperscript{61} with $U = 8.0$ eV and $\kappa_{i,j} = 2.0$ ($i \neq j$) and $\kappa_{i,i} = 1.0$. The screened parameters employed here were originally devised by Chandross and Mazumdar\textsuperscript{61} with the aim of accounting for the inter chain screening effects in phenylene based polymers. However, they can also be seen to account for the effect of the host in solution or thin-film based experiments.

The starting point of the correlated calculations for the molecules is the Restricted Hartree-Fock (RHF) calculations, employing the PPP Hamiltonian, using a code developed in our group.\textsuperscript{62} All the resultant HF molecular orbitals are treated as active orbitals. The single-reference CI calculations such as the full/quadruple CI (FCI/QCI) were employed for shorter acenes, while the MRSDCI method was used for the longer ones. In particular, FCI method was used for naphthalene and anthracene, while the QCI and MRSDCI methods were employed for longer oligomers. The MRSDCI method is a well-established approach for including electron-correlation effects beyond the mean-field both for the ground and excited states of molecular systems.\textsuperscript{63,64} In this approach, the CI matrix is constructed by generating singly and doubly excited configurations with respect to a given set of reference configurations which are specific to the states being targeted in the calculation. The calculations are performed in an iterative manner until acceptable convergence has been achieved. We have used this methodology extensively within the PPP model to study the optical properties of a number of conjugated polymers,\textsuperscript{6,16,59,65–67} and refer the reader to those papers for the technical details associated with the approach.
III. RESULTS AND DISCUSSIONS

Table I. The sizes of the CI matrix diagonalized, for different symmetries of oligoacenes (acene-\( n \)) of increasing length, \( n \). Below std and scr refer to standard and screened parameters, respectively. Superscripts \( a, b, \ldots \) etc. refer to the type of CI calculations performed, and are explained below.

| \( n \) | \( 1A_g^- \) | \( 1B_{2u}^+ \) | \( 3B_{2u}^+ \) | \( 3A_g^- \) | \( 3B_{1g}^- \) |
|---|---|---|---|---|---|
| 2 | 4936\(^a\) | 4794\(^a\) | 7370\(^a\) | 7360\(^a\) | 7440\(^a\) |
| 3 | 623576\(^a\) | 618478\(^a\) | 1099182\(^a\) | 1106140\(^a\) | 1104544\(^a\) |
| 4 | 193538\(^b\) | 335325\(^b\) | 614865\(^b\) | 201879\(^c\) | 217203\(^c\) |
|   |   |   |   | 224735\(^c\) | 224266\(^c\) |
| 5 | 1002597\(^b\) | 1707243\(^b\) | 3202299\(^b\) | 582278\(^c\) | 490532\(^c\) |
|   |   |   |   | 621397\(^d\) | 531551\(^d\) |
| 6 | 3940254\(^b\) | 6434183\(^b\) | 12234931\(^b\) | 1231948\(^c\) | 1156916\(^c\) |
|   |   |   |   | 1443726\(^d\) | 1107262\(^d\) |
| 7 | 12703819\(^b\) | 19663495\(^b\) | 37724739\(^b\) | 2414274\(^c\) | 1848466\(^c\) |
|   |   |   |   | 2611198\(^d\) | 1795626\(^d\) |

\(^a\)FCI  
\(^b\)QCI  
\(^c\)MRSDDCI (std)  
\(^d\)MRSDDCI (scr)

Before discussing our results, in table I we present the dimensions of the CI matrices employed for calculating the ground and excited states of different symmetries, for oligoacenes of increasing lengths. We note that the largest QCI calculation performed on heptacene involved dimension in excess of thirty seven million configurations. Thus, given the large-scale nature of these calculations, we are confident that electron-correlation effects have been accounted for in any adequate manner. Because of the large dimensions of these matrices, typically lowest 50–70 of their eigenroots were computed using Davidson algorithm as implemented in the MELD program.\(^{68}\) In spite of this restriction in the number of computed eigenvectors, the energy region covered for computing the absorption spectra was sufficiently large so as to allow comparison of our results with the experiments in a broad spectral range.
Figure 2. Diagram of the essential states involved in the triplet excited state absorption in oligoacenes and their polarization characteristics. The arrows connecting two states imply optical absorption, with polarization directions stated next to them. Location of states is not up to scale. ISC refers to inter-system crossing.

Triplet excited state absorption can be explained by means of a schematic diagram shown in Fig. 2. Light absorption takes place from $1^3B_{2u}^+$ ($T_1$) state through long-axis ($x$) or short-axis ($y$) polarized photons leading the system to $3^1B_{1g}^-$ or $3^1A_g^-$ type excited states. As far as the energetics of various excited states are concerned, our results are summarized in Tables II and III, where experimental and theoretical results obtained by other authors are also presented. In triplet absorption experiments, the excitation energies are measured with respect to the reference $1^3B_{2u}^+$ state. Therefore, to keep the comparison with the experiments transparent, in Tables II and III we present the energies of $3^1B_{1g}^-$ or $3^1A_g^-$ type excited states with respect to the $1^3B_{2u}^+$ state. However, excitation energies of these states with respect to the $1^1A_g^-$ ground state are presented in various tables in the Appendix.

A. Energies of Triplet States

Before discussing the cases of individual oligomers, first we make a few general comments about the results presented in Tables II and III. As far as the excitation energy of first triplet excited state $1^3B_{2u}^+$ state is concerned, our standard parameter based results are in better agreement with the experiments as compared to the screened parameter ones, for
naphthalene, anthracene and tetracene. From pentacene onwards, the results obtained with the two parameter sets tend to merge, however, experimental results are not available for the $1^3B_{2u}^+$ state of heptacene.

Other important triplet states for oligoacenes are $1^3B_{1g}^+$, $1^3A_{1g}^+$, $1^3B_{1g}^-$, and $1^3A_{1g}^-$. Of these, optical transitions to $1^3B_{1g}^+$ and $1^3A_{1g}^+$ from the $1^3B_{2u}^+$ state are dipole forbidden within the PPP model, because of the particle-hole symmetry inherent in the system due to the nearest-neighbor hopping approximation. In reality, of course, particle-hole symmetry is approximate, and, therefore, these states are faintly visible in the excited state absorption from the $T_1$. Even though in our calculations these states are absent in the computed spectra, nevertheless, it is possible to identify them by examining their many-particle wave functions.

Our calculated values of the excitation energies of the dipole forbidden state $1^3B_{1g}^+$ obtained using both sets of Coulomb parameters are in good qualitative agreement with each other, although, quantitatively speaking, the standard parameter values are slightly larger than the screened parameter ones. As far as the experiments are concerned, the values of $E(1^3B_{1g}^+) - E(1^3B_{2u}^+)$ are available only for naphthalene, anthracene, and tetracene, and in those cases our calculated results appear to be slightly lower than the experimental values. Similar trends hold for the other dipole forbidden state, $1^3A_{1g}^+$ as well, except that the standard parameter value of $E(1^3A_{1g}^+) - E(1^3B_{2u}^+)$ for tetracene is in excellent agreement with the experimental ones.

As far as the theoretical values of $E(1^3A_{1g}^+) - E(1^3B_{2u}^+)$, an interesting trend emerges irrespective of the parameters used, in that with the increasing length of the oligomers up to pentacene, this excitation energy increases. Experimentally speaking, a similar trend is visible for all the oligomers up to tetracene, while for the longer oligomers, the experimental values are not available. This counterintuitive trend in the values of $E(1^3A_{1g}^+) - E(1^3B_{2u}^+)$, with respect to the oligomer lengths, suggests that $1^3A_{1g}^+$ state is much more localized than the $1^3B_{2u}^+$ state because of which the decrease in the value of $E(1^3A_{1g}^+)$, with the increasing oligomer length, is slower as compared to $E(1^3B_{2u}^+)$. Therefore, it will be of tremendous interest to measure this value for longer acenes as well, so that this theoretical prediction of ours can be tested.

For the dipole allowed state $1^3B_{1g}^-$, the excitation energies computed by the standard parameters are larger than those computed by screened parameters for all the oligomers.
Experimental values of these excitation energies are available for all the oligoacenes considered here, and, on the average, much better agreement is found with the screened parameter results.

For the $1^3A_g^-$ state, however, screened parameter values of the excitation energies are larger compared to the standard ones for naphthalene, anthracene, and tetracene (cf. Table II), almost equal for pentacene, and smaller for hexacene and heptacene ((cf. Table III). Experimental values of $E(1^3A_g^-) - E(1^3B_{2u}^+)$ are available up to pentacene, and, they have disagreements amongst themselves for naphthalene and tetracene for which multiple values have been reported. Overall, the experimental results are in good agreement with the theory, except for the case of pentacene, for which theoretical values are larger than the measured one.

Next, we present a comparison of our results for individual oligomers with the theoretical works of other authors, as well as with the experiments.

1. Naphthalene

For naphthalene and anthracene FCI calculations have been performed which yield exact results within the chosen model Hamiltonian, and, therefore, cannot be improved. Thus, any discrepancy in the results with respect to the experiments has to be understood as a limitation of the PPP model, or the parameters used to describe it.

Since we have performed calculations on isolated oligomers, therefore, most appropriate comparison will be with the experiments performed in the gas or liquid solution phase.

Lewis and Kasha,$^{17}$ and McClure,$^{18}$ based upon their solution based experiments reported the value of $E(1^3B_{2u}^+)$ of naphthalene to be 2.64 eV. Exactly the same value was also reported by Swiderek et al.$^{46}$ based upon electron-energy loss spectroscopy measurements of naphthalene deposited on solid argon thin films. This value is in very good agreement with our standard parameter based value of 2.53 eV, but is significantly larger than the screened parameter value of 2.11 eV. As far as comparison with other theoretical works goes, our standard parameter value of $E(1^3B_{2u}^+)$ is in almost perfect agreement with the PPP-FCI value
Table II. Comparison of results of our triplet calculations for naphthalene, anthracene, and tetracene, performed using the standard (std.)/screened (scr.) parameters in PPP model, with other experimental and theoretical results for the most important low-lying states. As explained in the text, energies of the excited states of $3B_{1g}$ and $3A_g$ type, are given with respect to the $1^3B_{2u}^+$ state.

| State | Excitation energy (eV) | Present work | Experimental | Other theoretical |
|-------|------------------------|--------------|--------------|-------------------|
|       |                        | std. | scr. |                 |                 |
| Naphthalene (C$_{10}$H$_8$) | | | | |
| $1^3B_{2u}^+$ | 2.53 | 2.11 | 2.64(1)$^{17,18,46}$ | 2.52,$^{69}$2.72,$^{53}$2.18,$^{40}$2.71,$^{54}$2.67,$^{52}$2.98,$^{46}$3.05,$^{48}$ |
| $1^3B_{1g}^+$ | 1.21 | 1.16 | 1.30-1.35(1)$^{21}$ | 1.18,$^{41}$1.24,$^{40}$1.10,$^{46}$1.14$^{48}$ |
| $1^3A_g^+$ | 2.06 | 1.97 | 1.97(1),$^{21}$2.25(g)$^{20}$ | 2.03,$^{41}$2.25,$^{40}$2.01,$^{46}$2.18$^{48}$ |
| $1^3B_{1g}^-$ | 3.60 | 3.50 | 3.12(g),$^{19,23}$2.98(l),$^{26}$3.00(l)$^{21}$ | 3.29,$^{41}$3.52,$^{40}$3.24,$^{46}$2.61,$^{48}$2.71$^{49}$ |
| $1^3A_g^-$ | 3.76 | 4.12 | 2.93(g),$^{20}$3.63(l),$^{26}$3.10(l)$^{21}$ | 3.35,$^{41}$3.63,$^{40}$2.76,$^{46}$2.81,$^{48}$2.92$^{49}$ |
| Anthracene (C$_{14}$H$_{10}$) | | | | |
| $1^3B_{2u}^+$ | 1.73 | 1.48 | 1.82(l),$^{17,18}$1.87(g)$^{70}$ | 1.72,$^{43}$2.0,$^{53}$1.8,$^{55}$1.66,$^{40}$1.81,$^{54}$1.99,$^{52}$1.45$^{45}$ |
| $1^3B_{1g}^+$ | 1.22 | 1.10 | 1.40(l)$^{21}$ | 1.18,$^{40}$1.35$^{49}$1.42,$^{45}$ |
| $1^3A_g^+$ | 2.31 | 2.11 | 2.65(l),$^{26}$2.40(l)$^{21}$ | 2.32,$^{40}$2.62,$^{49}$3.70$^{45}$ |
| $1^3B_{1g}^-$ | 3.30 | 3.09 | 3.24(g),$^{21}$3.07(g),$^{23}$2.92(l)$^{21,26}$ | 3.35,$^{45}$3.28,$^{40}$4.65,$^{42}$2.74$^{50}$ |
| $1^3A_g^-$ | 3.84 | 3.96 | 3.77(l)$^{21}$ | 4.16,$^{45}$3.32,$^{40}$4.24,$^{42}$3.03$^{50}$ |
| Tetracene(C$_{18}$H$_{12}$) | | | | |
| $1^3B_{2u}^+$ | 1.25 | 1.11 | 1.25(s)$^{71}$1.27(l),$^{22}$1.30(l)$^{25}$ | 1.22,$^{14}$1.39,$^{53}$1.12,$^{55}$1.33,$^{72}$1.10,$^{40}$1.20,$^{54}$1.51$^{52}$ |
| $1^3B_{1g}^+$ | 1.09 | 1.04 | 1.29(l)$^{21}$ | 1.24,$^{45}$0.763,$^{40}$0.92,$^{50}$ |
| $1^3A_g^+$ | 2.55 | 2.42 | 2.58(l),$^{21}$3.12.60(l)$^{26}$ | 2.65,$^{40}$2.93$^{50}$ |
| $1^3B_{1g}^-$ | 3.05 | 2.79 | 2.92(g),$^{23}$2.69(l),$^{26}$2.68(l),$^{21}$2.55(l)$^{27}$ | 3.07,$^{44}$2.97,$^{15}$3.16,$^{40}$2.51$^{50}$ |
| $1^3A_g^-$ | 3.82 | 3.91 | 3.95(l),$^{26}$3.66(l),$^{21}$3.01(l)$^{27}$ | 3.82,$^{44}$1.23,$^{45}$3.39,$^{40}$3.26$^{50}$ |

of 2.52 eV reported by Ramasesha and Soos,$^{69}$ and in good agreement with the CCSDT(T) value of 2.72 eV reported by Hajgato et al.,$^{53}$ first-principles DMRG value of 2.67 eV reported by Hachmann et al.$^{52}$ and 2.71 eV reported by Houk et al.$^{54}$ computed using the B3LYP as exchange-correlation functional with a 6-31G* basis sets. Swiderek et al.$^{46}$ reported a
Table III. Comparison of results of our triplet calculations for pentacene, hexacene, and heptacene \((n = 5 - 7)\) performed with the standard (std.) parameters and the screened (scr.) parameters with other experimental and theoretical results for the most important low-lying states. The energies of the \(1^3B_{1g}^-\) and \(1^3A_g^-\) states are given with respect to the \(1^3B_{2u}^+\) state.

| State       | Excitation energy (eV) | Present work | Experimental | Other theoretical |
|-------------|------------------------|--------------|--------------|-------------------|
|             |                        | std.         | scr.         |                   |
| Pentacene\((C_{22}H_{14})\) |                         |              |              |                   |
| \(1^3B_{2u}^+\) | 0.99                  | 0.93         | 0.95(l)      | 0.86\(\pm\)0.03(s)\)\(^{28}\) 0.53,\(^{45}\) 0.91,\(^{43}\) 1.05,\(^{52}\) 0.99,\(^{33}\) 0.88,\(^{51}\) 0.99,\(^{72}\) 0.79,\(^{40}\) 0.78,\(^{54}\) 1.16\(^{52}\) |
| \(1^3B_{1g}^+\) | 0.96                  | 0.90         |              | \(0.88,\(^{40}\) 1.06,\(^{45}\) 1.24\(^{51}\) |
| \(1^3A_g^+\) | 2.67                  | 2.44         |              | 2.90,\(^{40}\) 4.15\(^{45}\) |
| \(1^3B_{1g}^-\) | 2.87                  | 2.54         | 2.53(l),\(^{26}\) 2.46(l)\(^{29}\) | 2.76,\(^{45}\) 2.89\(^{40}\) |
| \(1^3A_g^-\) | 3.77                  | 3.79         | 3.16(l)\(^{29}\) | 4.40,\(^{45}\) 3.43,\(^{40}\) |
| Hexacene\((C_{26}H_{16})\) |                         |              |              |                   |
| \(1^3B_{2u}^+\) | 0.87                  | 0.85         | 0.54\(\pm\)0.05(l)\(^{30}\) | 0.73,\(^{58}\) 0.46,\(^{54}\) 0.45,\(^{74}\) 0.91\(^{52}\) |
| \(1^3B_{1g}^+\) | 0.80                  | 0.75         |              |                   |
| \(1^3A_g^+\) | 2.63                  | 2.25         |              |                   |
| \(1^3B_{1g}^-\) | 2.70                  | 2.33         | 2.25(l)\(^{30}\) | 2.18,\(^{57}\) 2.42\(^{30}\) |
| \(1^3A_g^-\) | 3.74                  | 3.65         |              |                   |
| Heptacene\((C_{30}H_{18})\) |                         |              |              |                   |
| \(1^3B_{2u}^+\) | 0.73                  | 0.69         |              | 0.54,\(^{53}\) 0.24\(^{54}\) |
| \(1^3B_{1g}^+\) | 0.69                  | 0.61         |              |                   |
| \(1^3A_g^+\) | 2.34                  | 1.90         |              |                   |
| \(1^3B_{1g}^-\) | 2.58                  | 2.14         | 2.14(l)\(^{12}\) |                   |
| \(1^3A_g^-\) | 3.72                  | 3.17         |              |                   |

much larger value of 2.98 eV based upon the CNDO/S-CI method. Whereas our screened parameter value of 2.11 eV for \(E(1^3B_{2u}^+)\), is more in accordance with the earlier value of 2.18 eV reported by Pariser,\(^{40}\) computed using the PPP-SCI method.

For the dipole forbidden state \(1^3B_{1g}^+\), Meyer et al.,\(^{21}\) based upon their solution based experiment, reported \(E(1^3B_{1g}^+) - E(1^3B_{2u}^+)\) to be in the range 1.30-1.35 eV, a value which
is in good agreement with our standard parameter based value of 1.21 eV. Our screened parameter value 1.16 eV underestimates the experimental value somewhat. Other reported theoretical values for this quantity are 1.10 eV computed using the CNDO/S-CI by Swiderek et al.,\textsuperscript{46} 1.14 eV calculated using the CASPT2 approach,\textsuperscript{48} 1.18 eV computed by de Groot and Hoytink\textsuperscript{41} using the PPP-CI method, and 1.24 eV by Pariser,\textsuperscript{40} using the PPP-SCI approach.

For the state $1^3A_g^+$, there are two reported experimental values of $E(1^3A_g^+) - E(1^3B_{2u}^+)$, 1.97 eV\textsuperscript{21} based upon the solution phase data, and 2.25 eV obtained by Hunziker\textsuperscript{20} from the gas phase experiments. Our screened parameter value of 1.97 eV matches exactly with the solution phase results,\textsuperscript{21} while the standard parameter value of 2.06 eV is in between the two experimental values. As far as the theoretical works of other authors are concerned, using the CNDO/S-CI method Swiderek et al.\textsuperscript{46} computed it to be 2.01 eV, PPP-CI approach of de Groot and Hoytink\textsuperscript{41} yielded the value 2.03 eV, Rubio et al.\textsuperscript{48} obtained 2.18 eV using the CASPT2 approach, while 2.25 eV was reported by Pariser,\textsuperscript{40} obtained from the PPP-SCI approach.

For the long-axis polarized dipole allowed state $1^3B_{1g}^-$, the reported experimental values of $E(1^3B_{1g}^-) - E(1^3B_{2u}^+)$ are in the range 2.98—3.12 eV,\textsuperscript{19,21,23,26} while for the short-axis polarized $1^3A_g^-$ state the corresponding values fall in the range 2.93—3.63 eV.\textsuperscript{20,21,26} Our calculated values for $E(1^3B_{1g}^-) - E(1^3B_{2u}^+)$ 3.50 eV (screened parameters) and 3.60 eV (standard parameters) appear to overestimate corresponding experimental values. Reported theoretical values of other authors range from 2.61 eV to 3.52 eV (\textit{cf.} Table II), obtained using a variety of methods.\textsuperscript{40,41,46,48,49} For the $1^3A_g^-$ state, our standard parameter value 3.76 eV for $E(1^3A_g^-) - E(1^3B_{2u}^+)$ is in excellent agreement with 3.63 eV measured by Porter and Windsor\textsuperscript{26} in a solution based experiment. Other authors have reported theoretical values of this quantity in the range 2.76—3.63 eV,\textsuperscript{40,41,46,48,49} of which 3.63 eV reported by Pariser\textsuperscript{40} is in closest agreement with our standard parameter value.\textsuperscript{40}

2. \textit{Anthracene}

Like naphthalene, for anthracene also several experimental and theoretical investigations have been performed over the years. In early solution based experiments Lewis and Kasha,\textsuperscript{17} as well as McClure\textsuperscript{18} reported the value of $E(1^3B_{2u}^+)$ to be 1.82 eV, while in a more recent gas
phase experiment, Schiedt and Weinkauf\textsuperscript{70} measured it to be 1.87 eV. Here again the standard parameter value of 1.78 eV is in significantly better agreement with the experiments as compared to the screened parameter value of 1.48 eV. Similar to the case of naphthalene, even other theoretical calculations also match well with our standard parameter value. Ramasesha \textit{et al.}, based upon PPP-FCI calculations reported $E(1^3B_{2u}^+)$ as 1.71 eV,\textsuperscript{75} Houk \textit{et al.}\textsuperscript{54} based upon DFT calculations, and Quarti \textit{et al.}\textsuperscript{55} relying on a variety of quantum-chemical calculations reported it to be 1.8 eV, while Hachmann \textit{et al.}\textsuperscript{52} and Hajgato \textit{et al.}\textsuperscript{53} computed it as 2.0 eV.

For the dipole forbidden state $1^3B_{1g}^+$, the reported experimental value of $E(1^3B_{1g}^+)-E(1^3B_{2u}^+)$ 1.40 eV\textsuperscript{21} is closer to our standard parameter value 1.22 eV as compared to the screened parameter one. Theoretical works of other authors are in the range 1.18—1.42 eV,\textsuperscript{40,45,49} thus our standard parameter value lies in between the range. For the higher dipole forbidden state $1^3A_g^+$, two experimental values 2.40 eV\textsuperscript{21} and 2.65 eV\textsuperscript{26} based upon the liquid phase data have been reported, and both are in better agreement with our standard parameter value 2.31 eV, as compared to the screened one. Theoretical values reported by other authors for $E(1^3A_g^+)-E(1^3B_{2u}^+)$ are 2.32 eV,\textsuperscript{40} 2.62 eV,\textsuperscript{49} and 3.70 eV,\textsuperscript{45} of which the first two values are in good agreement with our standard parameter results.

For the dipole allowed state $1^3B_{1g}^-$, the value of $E(1^3B_{1g}^-)-E(1^3B_{2u}^+)$ from solution based experiments was reported to be 2.92 eV,\textsuperscript{21,26} while gas phase experiments report two distinct values 3.07 eV,\textsuperscript{23} and 3.24 eV.\textsuperscript{24} Interestingly, both our screened and standard parameter values are in good agreement with the two gas phase results. Theoretically speaking our standard parameter values are in good agreement with the works of Pariser,\textsuperscript{40} and Lipari and Duke.\textsuperscript{45}

For the short-axis polarized dipole allowed state $1^3A_g^-$, only available experimental value of $E(1^3A_g^-)-E(1^3B_{2u}^+)$ is 3.77 eV, measured in the solution phase.\textsuperscript{21} Our standard parameter value of 3.84 eV is in excellent agreement with this value, while the screened parameter value 3.96 eV overestimates it a bit. Other theoretical values of this quantity are distributed in the wide range 3.03—4.24 eV.\textsuperscript{40,42,45,50}
3. **Tetracene**

For tetracene, \( E(1^3B_{2u}^+) \) was measured in solid phase by Tomkiewicz *et al.*\(^{71} \) as 1.25 eV, and in liquid phase experiments Mc Glynn *et al.*\(^{22} \) obtained the value 1.27 eV, while Sabbatini *et al.*\(^{25} \) measured it to be 1.30 eV. These experimental values are in closer agreement with our standard parameter based value of 1.25 eV, as compared to the screened parameter value 1.11 eV. In a recent remarkable theoretical work, Pati and Ramasesha managed to perform PPP-FCI calculations for anthracene,\(^{44} \) and their \( E(1^3B_{2u}^+) \) value of 1.22 eV is in excellent agreement with our standard parameter result obtained using the QCI approach. Theoretical calculations by other authors predict this energy to be in the range 1.10—1.51 eV.\(^{40,52-55,72} \)

For the dipole forbidden state \( 1^3B_{1g}^+ \), only one reported experimental value of \( E(1^3B_{1g}^+) - E(1^3B_{2u}^+) \) is based upon liquid phase measurement. Our calculated values are lower than this, with the standard parameter value of 1.09 eV, being somewhat better than the screened parameter value 1.04 eV. Among the theoretical works of other authors, only the value 1.24 eV computed by Lipari and Duke\(^{45} \) is in better agreement with the experiments as compared to our results. For the other dipole forbidden state \( 1^3A_{g}^+ \), solution based measurements yield values of \( E(1^3A_{g}^+) - E(1^3B_{2u}^+) \) as 2.58 eV,\(^{21,31} \) and 2.60 eV,\(^{26} \) which are in close agreement with each other, and also with our standard parameter value 2.55 eV. Other reported theoretical values of this quantity overestimate the experiments (cf. Table II).

As in the case of anthracene, for the first dipole allowed state \( 1^3B_{1g}^- \), significant variation in the experimental values of \( E(1^3B_{1g}^-) - E(1^3B_{2u}^+) \) is observed. Porter and Wright\(^{23} \) measured it to be 2.92 eV in gas phase, which is in excellent agreement with our standard parameter value of 3.05 eV. However, the reported experimental values based upon liquid phase measurements 2.55 eV,\(^{27} \) 2.68 eV,\(^{21} \) and 2.69 eV,\(^{26} \) are, expectedly, in better agreement with our screened parameter value 2.79 eV. As far as theoretical results of other authors are concerned, recent PPP-FCI value 3.07 eV reported by Pati and Ramasesha\(^{44} \) is in excellent agreement with our standard parameter value, while other reported values in the literature fall in the range 2.51—3.16 eV.\(^{40,45,50} \)

For the higher dipole allowed state \( 1^3A_{g}^- \), even though all the experimental measurements of \( E(1^3A_{g}^-) - E(1^3B_{2u}^+) \) were performed in the liquid phase, yet they exhibit significant varia-
tion with reported values 3.01 eV, 3.66 eV, and 3.95 eV. Because of this variation, both our standard and screened parameter values are in good agreement with one experimental value or another (cf. Table II). As shown in Table II, theoretical values of this quantity computed by other authors also exhibit wide variation, with our standard parameter results being in perfect agreement with the PPP-FCI values reported by Pati and Ramasesha.44

4. Pentacene

Pentacene is one of the most widely studied polyacene, and extremely important from the point of view of singlet fission problem, currently being studied vigorously. Nijegorodov et al. measured the value of \( E(1^3B_{2u}^+) \) to be 0.95 eV in a liquid phase experiment, while Burgos et al. obtained it to be 0.86 eV in a solid phase experiment. Both our standard parameter value 0.99 eV, and screened parameter value of 0.93 eV, are in good agreement with the liquid phase measurement. Furthermore, quite expectedly, the screened parameter value is closer to the solid state measurement as compared to the standard parameter result. A large number of theoretical calculations have been performed for this quantity for pentacene, and they range from a low value of 0.53 eV obtained in a CNDO/S2-CI calculation, to a high value of 1.16 eV obtained from a DMRG calculation. However, several other calculations predict values in good agreement with our work, and with the experiments.

To the best of our knowledge, no experimental measurements of the dipole forbidden states \( 1^3B_{1g}^+ \) and \( 1^3A_g^+ \) exist for pentacene, therefore, we will restrict the comparison of our results on these states to the theoretical works of other authors. Pariser computed the value of \( E(1^3B_{1g}^+) - E(1^3B_{2u}^+) \) to be 0.88 eV, while Lipari and Duke predicted it to be 1.06 eV, both of which are in reasonable agreement with our computed values. The value 1.24 eV computed by Zimmerman et al. for the quantity is substantially larger than our prediction. For the \( 1^3A_g^+ \) state our calculated values of \( E(1^3A_g^+) - E(1^3B_{2u}^+) \) 2.44 eV (screened), and 2.67 eV (standard), are lower compared to the PPP-SCI value 2.90 eV reported by Pariser, but significantly smaller compared to 4.15 eV calculated by Lipari and Duke. Given the uncertainty in the theoretical excitation energies of these dipole forbidden states, it will be good if measurements are performed on these states of pentacene in future.

For the long-axis polarized dipole-allowed state \( 1^3B_{1g}^- \), two liquid phase experimental values of \( E(1^3B_{1g}^-) - E(1^3B_{2u}^+) \) 2.46, and 2.53 are in excellent agreement with our calculated
screened parameter value 2.54 eV, while the standard parameter approach predicts a larger value. Theoretical calculations by other authors\textsuperscript{40,45} (cf. Table III) predict values larger than the experimental one, and are in better agreement with our standard parameter calculation. For the other dipole allowed state $1^3A_g^-$, we have an anomaly vis-a-vis experiments in that the only available experimental value of $E(1^3A_g^-) - E(1^3B_{2u}^+)$ 3.16 eV,\textsuperscript{29} is substantial smaller than all the calculated theoretical values, including our own. Therefore, it will be quite useful if an experiment could be repeated on pentacene to ascertain the excitation energy of this state.

5. Hexacene and Heptacene

Very few experiments have been performed on the triplet states of higher acenes such as hexacene and heptacene, perhaps because of difficulties associated with their synthesis. As a result, the number of theoretical calculations on these compounds are relatively small. For hexacene, based on a liquid phase experiment, Angliker \textit{et al.}\textsuperscript{30} estimated the value of $E(1^3B_{2u}^+)$ to be 0.54 eV, which is substantially smaller than our computed values 0.85 eV (screened) and 0.87 eV (standard). This reported experimental value is also not in agreement with the theoretical works of other authors whose values are either significantly smaller than it, or larger than it (cf. Table III). In the same experiment, Angliker \textit{et al.}\textsuperscript{30} measured $E(1^3B_{1g}^-) - E(1^3B_{2u}^+)$ to be 2.25 eV which is actually in very good agreement with our screened parameter value 2.33 eV. Angliker \textit{et al.}\textsuperscript{30} also calculated the value of this excitation energy using the PPP-SCI approach using a different set of Coulomb parameters, and obtained the value 2.42 eV, which is in good agreement with our screened parameter result. DFT based calculations of Nguyen \textit{et al.}\textsuperscript{57} predict the value of this energy as 2.18 eV, which is close to the experimental value, but somewhat smaller than our screened parameter result.

For heptacene, to the best of our knowledge, no experimental measurements of $E(1^3B_{2u}^+)$ exist. Theoretical calculations by Hajgato \textit{et al.}\textsuperscript{53} predict it to be 0.54 eV, while the DFT based work of Houk \textit{et al.}\textsuperscript{54} estimates a rather small value of 0.24 eV. From Table III it is obvious that our calculated values are larger than these results, with a somewhat better agreement between the work of Hajgato \textit{et al.}\textsuperscript{53} and our screened parameter estimate. However, liquid phase experimental measurements on the dipole allowed $1^3B_{1g}^-$ state of
heptacene were carried out by Mondal et al.\textsuperscript{12} who measured $E(1^3B_{1g}^-) - E(1^3B_{2u}^+)$ to be 2.14 eV, which is in exact agreement with our screened parameter result, thus giving us confidence about the quality of our calculations even for a relatively longer oligoacene such as heptacene.

B. Triplet Absorption Spectrum

In optical absorption experiments, one can probe the triplet excited states because frequently the first singlet excited state $S_1$ ($1^1B_{2u}^+$, in the present case) decays to the first triplet excited state $T_1$ ($1^3B_{2u}^+$, in the present case) located below $S_1$, through nonradiative inter-system crossing (ISC), as shown in Fig. 2. In case of single crystals or thin films, this transition is believed to occur via singlet fission\textsuperscript{32} whose mechanism is also an area of intense research.\textsuperscript{4,5} Once the system reaches the triplet manifold, normal optical absorption experiments can be performed to probe higher triplet states. For the case of oligoacenes, as per electric-dipole selection rules of the $D_{2h}$ point group, the long-axis ($x$-axis) polarized photons cause transitions from the $1^3B_{2u}^+$ to $3^3B_{1g}^-$ type of states, while the short-axis ($y$-axis) polarized ones lead to the $3^3A_{g}^-$ type states (\textit{cf.} Fig. 2). Figs. 3—8 present the excited state absorption spectra of naphthalene to heptacene, while the wave functions of the excited states contributing to various peaks in spectra, along with the corresponding dipole moments, are presented in Tables IV—XV of the Appendix.

The triplet excited state absorption of all the oligomers contains following general features:

1. Quantitatively speaking, screened parameter spectra are red shifted as compared to the standard parameter ones.

2. Most of the intensity is concentrated in the $x$-polarized (long-axis polarized) spectra corresponding to the absorption into the $3^3B_{1g}^-$ type of states, while the $y$—polarized absorption into the $3^3A_{g}^-$ type states is very faint.

3. From Figs. 3—8, it is obvious that the triplet absorption spectrum is dominated by two intense $x$—polarized peaks which are well separated in energy ($>1.5$ eV), irrespective of the oligoacene in question, or the Coulomb parameters employed in the calculations. The first of these peaks is peak I in all the cases, while the second one is peak III, IV
or V, depending upon the oligoacene, or the Coulomb parameters employed. Peak I is always the second most intense peak, while the second of these peaks (III, IV, or V) is the most intense irrespective of the choice of Coulomb parameters. Peak I always corresponds to the $1^3B_{1g}^-$ excited state of the system. If we adopt the notation such that $H$ denotes the highest occupied molecular orbital (HOMO), and $L$ denotes the lowest unoccupied molecular orbital (LUMO), then many-particle wave function of the state $1^3B_{1g}^-$ is dominated by singly-excited configurations $|H \rightarrow L + 2\rangle + c.c.$ ($c.c.$ denotes the charge-conjugated configuration) for the case of naphthalene and anthracene, while the single excitations $|H \rightarrow L + 1\rangle + c.c.$ dominate the wave function from tetracene up to heptacene, irrespective of the choice of Coulomb parameters. The second intense peak (III, IV, or V) corresponds to a higher $3^1B_{1g}$ type state of acene-$n$, whose wave function mainly consists of double excitations $|H \rightarrow L; H - n/2 \rightarrow L\rangle + c.c.$ for $n \equiv$ even, and $|H \rightarrow L; H - (n - 1)/2 \rightarrow L\rangle + c.c.$, for the $n \equiv$ odd, irrespective of the choice of the Coulomb parameters.

4. Other peaks in the spectrum correspond to either $x$ or $y$ polarized transitions to the higher excited states of the system, information about which is presented in the tables in the Appendix.

5. The lowest dipole forbidden states, $x$-polarized $1^3B_{1g}^+$, and $y$-polarized $1^3A_g^+$, are dominated by single excitations. Similar to $1^3B_{1g}^-$, the $1^3B_{1g}^+$ state has dominant contributions from $|H \rightarrow L + 2\rangle$ and $c.c.$ for naphthalene and anthracene, and from single excitations $|H \rightarrow L + 1\rangle$ and $c.c.$ for tetracene up to heptacene, irrespective of the choice of Coulomb parameters. The $y$-polarized $1^3A_g^+$ state has dominant contributions from excitations $|H \rightarrow L + 3\rangle + c.c.$ for the case of naphthalene and anthracene, from the single excitations $|H \rightarrow L + 4\rangle + c.c.$ for tetracene up to hexacene, but from double excitation $|H \rightarrow L; H - 1 \rightarrow L + 1\rangle$, for heptacene, irrespective of the choice of Coulomb parameters. Dominant contribution from double excitation also points to the increased electron-correlation effects.

As mentioned above, in the triplet absorption spectra for the oligoacenes up to heptacene (cf. Figs. 3—8), the second major peak (peak III, IV, or V) is the most intense one, while the first peak is always the second most intense peak, irrespective of the choice of the Coulomb parameters. This trend is contrary to what is observed in the longer acenes such
as octacene, nonacene and decacene, as discussed in our earlier paper,\textsuperscript{59} for which the first intense $x$–polarized state is of the highest intensity, while peak III always corresponds to the second most intense peak.

Figure 3. Excited state absorption spectra of naphthalene from the $1^3B_{2u}^+$ state computed using: (a) standard parameters, and (b) screened 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 $y$.

Figure 4. Excited state absorption spectra of anthracene from the $1^3B_{2u}^+$ state computed using: (a) standard parameters, and (b) screened parameters. The rest of the information is same as in the caption of Fig. 3.
Figure 5. Excited state absorption spectra of tetracene from the $1^3B_{2u}^+$ state computed using: (a) standard parameters, and (b) screened parameters. The rest of the information is same as in the caption of Fig. 3.

Figure 6. Excited state absorption spectra of pentacene from the $1^3B_{2u}^+$ state computed using: (a) standard parameters, and (b) screened parameters. The rest of the information is same as in the caption of Fig. 3.
Figure 7. Excited state absorption spectra of hexacene from the $1^3B_{2u}^+$ state computed using: (a) standard parameters, and (b) screened parameters. The rest of the information is same as in the caption of Fig. 3.

Figure 8. Excited state absorption spectra of heptacene from the $1^3B_{2u}^+$ state computed using: (a) standard parameters, and (b) screened parameters. The rest of the information is same as in the caption of Fig. 3.
C. Comparison with poly-(para)phenylene vinylene chains

Several years back, one of us performed a systematic study of triplet states and triplet optical absorption in oligomers of poly-(para)phenylene vinylene (PPV).\textsuperscript{6} Next we compare our earlier results on PPV with the present ones on oligoacenes. In finite PPV chains excitation energy of $T_1$ (1$^3B_u^+$ state) exhibited almost complete saturation starting from the two-unit oligomer, implying that $T_1$ is highly localized in PPV, and essentially has a Frenkel exciton character.\textsuperscript{6} However, it is obvious from Tables II and III, and also from our earlier work on longer acenes,$^5$\textsuperscript{9} that the excitation energy of $T_1$ (1$^3B_{2u}^+$) for oligoacenes exhibits no signs of saturation with increasing length, implying that, if $T_1$ for polyacene is an exciton in the thermodynamic limit, it is a highly delocalized one, similar to a Wannier exciton. In an earlier work, Shimoi and Mazumdar$^7$ had argued that the $m^3A_g$ state of conjugated polymers, which is the first excited state with a strong dipole coupling to $T_1$, is also an exciton, and, therefore, the quantity $E(m^3A_g) - E(1^1B_u)$ can serve as a lower-limit estimate of the binding energy of the optical exciton ($1^1B_u$). For the case of oligoacenes the first optical state is 1$^1B_{2u}^+$, while $m^3A_g$ is the 1$^3B_{1g}^-$ state. Therefore, using the values of $E(1^3B_{1g}^-)$ computed in this work, and $E(1^1B_{2u})$ calculated in our earlier work,$^1$\textsuperscript{6} for heptacene we obtain the values of $E(m^3A_g) - E(1^1B_u)$ to be 0.68 eV (standard) and 0.59 eV (screened). Our screened parameter value of 0.59 eV obtained for polyacenes is lower than 0.68 eV which we estimated for PPV using the same Coulomb parameters in the PPP model.\textsuperscript{6} Furthermore, if we examine the behavior of $E(m^3A_g) - E(1^1B_u)$ as a function of the length of oligoacene, with both sets of Coulomb parameters a decreasing trend is observed. Therefore, it will be of considerable interest to know whether, in the thermodynamic limit, exciton binding energy defined in this manner saturates to a finite value, or simply vanishes.

When we compare the triplet absorption spectra of PPV chains\textsuperscript{6} with those of oligoacenes, following differences emerge: \textit{(a)} the first peak in the absorption spectrum of PPV chains is always the most intense one, while in case of oligoacenes the first peak is always the second most intense peak, and \textit{(b)} successive peaks in case of PPV chains exhibit a pattern of alternating high and low intensities, while no such pattern is visible in case of oligoacenes.

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IV. CONCLUSION

In this work we presented large-scale electron-correlated calculations of the triplet states, as well as triplet-triplet absorption spectra, of oligoacenes ranging from naphthalene to heptacene. Generally very good agreement was observed between our calculations, and available experimental results. For the case of hexacene and heptacene, not much experimental data is available, therefore, our results on those oligomers could be tested in future experiments. As far as triplet absorption spectrum is concerned, our most important prediction is the presence of two long-axis polarized well-separated peaks, which we hope will be tested in future experiments on oriented samples of oligoacenes. We have also presented a detailed analysis of the wave functions of the important triplet excited states.

When compared to $T_1$ in PPV, our calculations find that the $T_1$ in oligoacenes is significantly delocalized, and has a Wannier exciton like character. Furthermore, we have observed that the triplet absorption spectra of polyacenes are qualitatively different as compared to those of the PPV chains. We have also presented numerical estimates of the optical exciton binding energy in oligoacenes, and found it to be less than that in PPV chains. However, these estimates can be significantly improved by performing calculations on longer oligoacenes. Moreover, it will also be of interest to probe the nonlinear optical properties of polyacenes, a topic which we intend to pursue in future works in our group.

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Appendix A: Calculated Energies, Wave Functions, and Transition Dipole Moments of the Excited States Contributing to the Triplet Absorption Spectra

In this section, we present Tables IV—XV which contain the excitation energies, transition dipole moments, and wave functions of the triplet excited states, which contribute to the
calculated triplet absorption spectra of oligoacenes ranging from naphthalene to heptacene, presented in Figs. 3—8 of the main text.

Table IV. Excited states contributing to the triplet absorption spectrum of naphthalene computed using the FCI 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. The excitation energies are with respect to the $1^1A_g^-$ ground state, while the dipole matrix elements are with respect to the $1^3B_{2u}^+$ 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. DF implies that the state in question is dipole forbidden.

| Peak | State | E (eV) | Transition | Dipole (Å) | dominant contributing configurations |
|------|-------|--------|------------|------------|--------------------------------------|
| DF   | $1^3B_{1g}^+$ | 3.74   | 0.0        |            | \[ H \to L + 2 \] − c.c.(0.6421) \[ H \to L + 3 \] + c.c.(0.1200) |
| DF   | $1^3A_g^+$  | 4.59   | 0.0        |            | \[ H \to L + 3 \] + c.c.(0.5355) \[ H \to L + 2 \] − c.c.(0.3475) |
| I    | $1^3B_{1g}^-$ | 6.13   | 0.739      |            | \[ H \to L + 2 \] + c.c.(0.6225) \[ H \to L + 1 \] − c.c.(0.2044) |
| II   | $1^3A_g^-$  | 6.29   | 0.225      |            | \[ H \to L + 2 \] + c.c.(0.5890) \[ H \to L + 3 \] − c.c.(0.2993) |
| III  | $2^3A_g^-$  | 7.3    | 0.590      |            | \[ H \to L + 3 \] − c.c.(0.5469) \[ H \to L + 2 \] + c.c.(0.2925) |
| IV   | $2^3B_{1g}^-$ | 7.9    | 0.608      |            | \[ H \to L + 3 \] − c.c.(0.5168) \[ H \to L + 1 \] − c.c.(0.2928) |
| V    | $3^3B_{1g}^-$ | 8.61   | 1.142      |            | \[ H \to L + 3 \] − c.c.(0.4939) \[ H \to L + 1 \] − c.c.(0.2839) |
Table V. Excited states contributing to the triplet absorption spectrum of naphthalene computed using the FCI method coupled with the screened parameters in the PPP model Hamiltonian. The rest of the information is same as in the caption of Table IV.

| Peak | State | E (eV) | Transition Dipole (Å) | dominant contributing configurations |
|------|-------|--------|----------------------|-------------------------------------|
| DF   | $1^3B^+_{1g}$ | 3.27   | 0.0                  | $| H \rightarrow L + 2 \rangle + c.c.(0.6148)$ |
|      |        |        |                      | $| H - 1 \rightarrow L + 3 \rangle - c.c.(0.1463)$ |
| DF   | $1^3A^+_{g}$ | 4.08   | 0.0                  | $| H \rightarrow L + 3 \rangle + c.c.(0.5349)$ |
|      |        |        |                      | $| H - 1 \rightarrow L + 2 \rangle - c.c.(0.2822)$ |
| I    | $1^3B^-_{1g}$ | 5.61   | 0.940                | $| H \rightarrow L + 2 \rangle - c.c.(0.6447)$ |
|      |        |        |                      | $| H \rightarrow L + 2; H - 3 \rightarrow L \rangle c.c.(0.1033)$ |
| II   | $1^3A^-_{g}$ | 6.23   | 0.182                | $| H - 1 \rightarrow L + 2 \rangle + c.c.(0.5731)$ |
|      |        |        |                      | $| H \rightarrow L + 3 \rangle - c.c.(0.3015)$ |
| III  | $2^3A^-_{g}$ | 6.48   | 0.579                | $| H \rightarrow L + 3 \rangle - c.c.(0.5535)$ |
|      |        |        |                      | $| H - 1 \rightarrow L + 2 \rangle + c.c.(0.2966)$ |
| IV   | $2^3B^-_{1g}$ | 7.16   | 0.234                | $| H - 1 \rightarrow L + 3 \rangle + c.c.(0.5873)$ |
|      |        |        |                      | $| H \rightarrow L; H \rightarrow L + 1 \rangle + c.c.(0.2220)$ |
| V    | $3^3B^-_{1g}$ | 7.75   | 1.109                | $| H \rightarrow L; H \rightarrow L + 1 \rangle + c.c.(0.5609)$ |
|      |        |        |                      | $| H - 1 \rightarrow L + 3 \rangle + c.c.(0.1903)$ |
| VI   | $3^3A^-_{g}$ | 8.47   | 0.466                | $| H \rightarrow L; H - 1 \rightarrow L + 1 \rangle (0.8268)$ |
|      |        |        |                      | $| H \rightarrow L + 3; H - 3 \rightarrow L \rangle (0.2105)$ |
Table VI. Excited states contributing to the triplet absorption spectrum of anthracene computed using the FCI method coupled with the standard parameters in the PPP model Hamiltonian. The rest of the information is same as in the caption of Table IV.

| Peak | State | E (eV) | Transition Dipole (Å) | dominant contributing configurations |
|------|-------|--------|-----------------------|-------------------------------------|
| DF   | $1^3B_{1g}^+$ | 2.95   | 0.0                   | $|H \rightarrow L + 2\rangle + c.c.(0.5992)$ |
|      |      |        |                       | $|H - 2 \rightarrow L + 4\rangle + c.c.(0.1889)$ |
| DF   | $1^3A^+_g$  | 4.04   | 0.0                   | $|H \rightarrow L + 3\rangle - c.c.(0.5106)$ |
|      |      |        |                       | $|H - 1 \rightarrow L + 2\rangle - c.c.(0.3024)$ |
| I    | $1^3B_{1g}^-$ | 5.03   | 1.132                 | $|H \rightarrow L + 2\rangle - c.c.(0.5986)$ |
|      |      |        |                       | $|H \rightarrow L; H \rightarrow L + 1\rangle + c.c.(0.1844)$ |
| II   | $1^3A^-_g$  | 5.57   | 0.356                 | $|H - 1 \rightarrow L + 2\rangle + c.c.(0.4912)$ |
|      |      |        |                       | $|H \rightarrow L + 3\rangle + c.c.(0.3989)$ |
| III  | $2^3A^-_g$  | 6.45   | 0.482                 | $|H \rightarrow L + 3\rangle + c.c.(0.4523)$ |
|      |      |        |                       | $|H - 1 \rightarrow L + 2\rangle + c.c.(0.3453)$ |
| IV   | $2^3B_{1g}^-$ | 6.95   | 1.568                 | $|H \rightarrow L; H \rightarrow L + 1\rangle + c.c.(0.5360)$ |
|      |      |        |                       | $|H - 1 \rightarrow L + 3\rangle - c.c.(0.1850)$ |
| V    | $3^3B_{1g}^-$ | 7.58   | 0.309                 | $|H - 1 \rightarrow L + 3\rangle - c.c.(0.3752)$ |
|      | $4^3A^-_g$  | 7.54   | 0.236                 | $|H \rightarrow L; H - 2 \rightarrow L + 2\rangle (0.5992)$ |
|      |      |        |                       | $|H \rightarrow L; H - 1 \rightarrow L + 1\rangle (0.5288)$ |
| VI   | $4^3B_{1g}^-$ | 7.83   | 0.356                 | $|H - 2 \rightarrow L + 4\rangle - c.c.(0.4031)$ |
|      |      |        |                       | $|H - 1 \rightarrow L + 3\rangle - c.c.(0.3235)$ |
Table VII. Excited states contributing to the triplet absorption spectrum of anthracene computed using the FCI method coupled with the screened parameters in the PPP model Hamiltonian. The rest of the information is same as in the caption of Table IV.

| Peak | State | E (eV) | Transition Dipole (Å) | dominant contributing configurations |
|------|-------|--------|-----------------------|-------------------------------------|
| DF   | $1^3B_{1g}^+$ | 2.58   | 0.0                   | $|H \rightarrow L + 2\rangle - c.c.(0.5735)$ |
|      |        |        |                       | $|H - 2 \rightarrow L + 4\rangle + c.c.(0.1776)$ |
| DF   | $1^3A_g^+$ | 3.59   | 0.0                   | $|H \rightarrow L + 3\rangle + c.c.(0.5042)$ |
|      |        |        |                       | $|H - 1 \rightarrow L + 2\rangle + c.c.(0.2449)$ |
| I    | $1^3B_{1g}^-$ | 4.57   | 1.394                 | $|H \rightarrow L + 2\rangle + c.c.(0.6219)$ |
|      |        |        |                       | $|H \rightarrow L; H - 1 \rightarrow L\rangle + c.c.(0.0854)$ |
| II   | $1^3A_g^-$ | 5.44   | 0.521                 | $|H \rightarrow L + 3\rangle - c.c.(0.5463)$ |
|      |        |        |                       | $|H - 1 \rightarrow L + 2\rangle - c.c.(0.2938)$ |
| III  | $2^3A_g^-$ | 5.72   | 0.370                 | $|H - 1 \rightarrow L + 2\rangle - c.c.(0.5371)$ |
|      |        |        |                       | $|H \rightarrow L + 3\rangle - c.c.(0.2765)$ |
| IV   | $2^3B_{1g}^-$ | 6.29  | 1.335                 | $|H \rightarrow L; H \rightarrow L + 1\rangle + c.c.(0.5577)$ |
|      |        |        |                       | $|H - 1 \rightarrow L + 3\rangle + c.c.(0.2127)$ |
| V    | $3^3B_{1g}^-$ | 6.78  | 0.544                 | $|H - 1 \rightarrow L + 3\rangle + c.c.(0.5194)$ |
|      |        |        |                       | $|H \rightarrow L; H \rightarrow L + 1\rangle + c.c.(0.1673)$ |
| VI   | $4^3A_g^-$ | 7.36   | 0.530                 | $|H \rightarrow L; H - 1 \rightarrow L + 1\rangle (0.5641)$ |
|      | $5^3A_g^-$ | 7.40   | 0.387                 | $|H \rightarrow L; H - 2 \rightarrow L + 2\rangle (0.4119)$ |
|      |        |        |                       | $|H \rightarrow L; H - 2 \rightarrow L + 2\rangle (0.6385)$ |
|      |        |        |                       | $|H \rightarrow L + 6\rangle - c.c.(0.3256)$ |
| VII  | $6^3A_g^-$ | 7.64   | 0.652                 | $|H \rightarrow L; H - 1 \rightarrow L + 1\rangle (0.7058)$ |
|      |        |        |                       | $|H - 3 \rightarrow L + 4\rangle + c.c.(0.2388)$ |

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Table VIII. Excited states contributing to the triplet absorption spectrum of tetracene computed using the MRSDCI method coupled with the standard parameters in the PPP model Hamiltonian. The rest of the information is same as in the caption of Table IV.

| Peak | State    | E (eV) | Transition Dipole (Å) | dominant contributing configurations |
|------|----------|--------|-----------------------|-------------------------------------|
| DF   | $1^3B_{1g}^+$ | 2.34   | 0.0                   | $|H \rightarrow L + 1\rangle - c.c.(0.5959)$ |
|      |          |        |                       | $|H - 1 \rightarrow L + 3\rangle + c.c.(0.1194)$ |
|      | $1^3A_g^+$ | 3.80   | 0.0                   | $|H \rightarrow L + 4\rangle - c.c.(0.4892)$ |
|      |          |        |                       | $|H - 1 \rightarrow L + 2\rangle + c.c.(0.3127)$ |
| I    | $1^3B_{1g}^-$ | 4.30   | 1.501                 | $|H \rightarrow L + 1\rangle + c.c.(0.5876)$ |
|      |          |        |                       | $|H \rightarrow L; H \rightarrow L + 2\rangle + c.c.(0.1630)$ |
| II   | $1^3A_g^-$   | 5.07   | 0.356                 | $|H - 1 \rightarrow L + 2\rangle - c.c.(0.4523)$ |
|      |          |        |                       | $|H \rightarrow L + 4\rangle + c.c.(0.4234)$ |
| III  | $3^3B_{1g}^-$ | 6.23   | 1.865                 | $|H \rightarrow L; H \rightarrow L + 2\rangle + c.c.(0.5446)$ |
|      |          |        |                       | $|H - 1 \rightarrow L; H \rightarrow L + 4\rangle c.c.(0.1402)$ |
| IV   | $3^3A_g^-$   | 6.59   | 0.346                 | $|H \rightarrow L; H - 1 \rightarrow L + 1\rangle (0.4758)$ |
|      |          |        |                       | $|H \rightarrow L; H \rightarrow L + 3\rangle + c.c.(0.4152)$ |
|      | $4^3A_g^-$   | 6.64   | 0.654                 | $|H \rightarrow L; H - 1 \rightarrow L + 1\rangle (0.6786)$ |
|      |          |        |                       | $|H \rightarrow L + 4\rangle + c.c.(0.1947)$ |
| V    | $6^3A_g^-$   | 7.39   | 0.239                 | $|H \rightarrow L; H - 1 \rightarrow L + 1\rangle (0.4877)$ |
|      |          |        |                       | $|H \rightarrow L; H - 2 \rightarrow L + 2\rangle (0.3882)$ |
Table IX. Excited states contributing to the triplet absorption spectrum of tetracene computed using the MRSDCI method coupled with the screened parameters in the PPP model Hamiltonian. The rest of the information is same as in the caption of Table IV.

| Peak | State | E (eV) | Transition Dipole (Å) | dominant contributing configurations |
|------|-------|--------|----------------------|-------------------------------------|
| DF   | $1^3B_{1g}^+$ | 2.15   | 0.0                  | $|H \rightarrow L + 1\rangle + c.c.(0.5828)$ |
|      |        |        |                      | $|H - 1 \rightarrow L + 3\rangle + c.c.(0.1199)$ |
| DF   | $1^3A_{g}^+$ | 3.53   | 0.0                  | $|H \rightarrow L + 4\rangle - c.c.(0.5092)$ |
|      |        |        |                      | $|H - 1 \rightarrow L + 2\rangle - c.c.(0.2542)$ |
| I    | $1^3B_{1g}^-$ | 3.90   | 1.824                | $|H \rightarrow L + 1\rangle - c.c.(0.6176)$ |
|      |        |        |                      | $|H \rightarrow L + 1; H - 1 \rightarrow L + 2\rangle c.c.(0.0735)$ |
| II   | $1^3A_{g}^-$ | 5.02   | 0.524                | $|H \rightarrow L + 4\rangle + c.c.(0.5638)$ |
|      |        |        |                      | $|H - 1 \rightarrow L + 2\rangle + c.c.(0.2617)$ |
| III  | $3^3B_{1g}^-$ | 5.78   | 1.648                | $|H \rightarrow L; H \rightarrow L + 2\rangle + c.c.(0.5793)$ |
|      |        |        |                      | $|H - 1 \rightarrow L; H - 2 \rightarrow L + 1\rangle c.c.(0.1355)$ |
| IV   | $4^3B_{1g}^-$ | 6.28   | 0.203                | $|H - 1 \rightarrow L + 3\rangle - c.c.(0.5696)$ |
|      | $3^3A_{g}^-$ | 6.31   | 0.779                | $|H \rightarrow L; H \rightarrow L; H - 1 \rightarrow L + 3\rangle - c.c.(0.1273)$ |
|      |        |        |                      | $|H \rightarrow L; H - 1 \rightarrow L + 1\rangle (0.8320)$ |
|      |        |        |                      | $|H \rightarrow L + 1; H - 1 \rightarrow L + 3\rangle - c.c.(0.1013)$ |
| V    | $7^3B_{1g}^-$ | 7.33   | 0.503                | $|H \rightarrow L; H - 2 \rightarrow L + 3\rangle - c.c.(0.3526)$ |
|      | $8^3A_{g}^-$ | 7.42   | 0.785                | $|H \rightarrow L; H - 2 \rightarrow L + 2\rangle (0.7912)$ |
|      |        |        |                      | $|H - 1 \rightarrow L + 2; H - 2 \rightarrow L + 1\rangle (0.1316)$ |
Table X. Excited states contributing to the triplet absorption spectrum of pentacene computed using the MRSDCI method coupled with the standard parameters in the PPP model Hamiltonian. The rest of the information is same as in the caption of Table IV.

| Peak | State  | E (eV) | Transition Dipole (Å) | dominant contributing configurations |
|------|--------|--------|-----------------------|-------------------------------------|
| DF   | $1^3B^+_{19}$ | 1.95   | 0.0                   | $|H \rightarrow L + 1\rangle - c.c.(0.5890)$ |
|      | $1^3A^-_g$   | 3.66   | 0.0                   | $|H \rightarrow L + 3\rangle - c.c.(0.1143)$ |
|      |           |        |                       | $|H \rightarrow L + 4\rangle - c.c.(0.4589)$ |
|      |           |        |                       | $|H - 1 \rightarrow L + 2\rangle + c.c.(0.3251)$ |
| I    | $1^3B^-_{19}$ | 3.86   | 1.842                 | $|H \rightarrow L + 1\rangle + c.c.(0.5785)$ |
|      |           |        |                       | $|H \rightarrow L; H \rightarrow L + 2\rangle + c.c.(0.1413)$ |
| II   | $1^3A^-_g$   | 4.76   | 0.303                 | $|H - 1 \rightarrow L + 2\rangle - c.c.(0.4328)$ |
|      |           |        |                       | $|H \rightarrow L + 4\rangle + c.c.(0.4179)$ |
| III  | $3^3B^-_{19}$| 5.84   | 2.02                  | $|H \rightarrow L; H \rightarrow L + 2\rangle + c.c.(0.5287)$ |
|      |           |        |                       | $|H - 1 \rightarrow L; H \rightarrow L + 4\rangle + c.c.(0.1615)$ |
| IV   | $3^3A^-_g$  | 6.09   | 0.373                 | $|H \rightarrow L; H - 1 \rightarrow L + 1\rangle (0.5984)$ |
|      | $4^3A^-_g$  | 6.15   | 0.706                 | $|H \rightarrow L; H \rightarrow L + 3\rangle - c.c.(0.3464)$ |
|      |           |        |                       | $|H \rightarrow L; H - 1 \rightarrow L + 1\rangle (0.3977)$ |
|      |           |        |                       | $|H \rightarrow L + 4\rangle + c.c.(0.3550)$ |
| V    | $6^3B^-_{19}$| 7.15   | 0.669                 | $|H \rightarrow L + 1; H - 4 \rightarrow L\rangle - c.c.(0.3978)$ |
|      |           |        |                       | $|H - 1 \rightarrow L + 2; H \rightarrow L + 1\rangle - c.c.(0.2217)$ |
Table XI. Excited states contributing to the triplet absorption spectrum of pentacene computed using the MRSDCI method coupled with the screened parameters in the PPP model Hamiltonian. The rest of the information is same as in the caption of Table IV.

| Peak | State | E (eV) | Transition | Dipole (Å) | dominant contributing configurations |
|------|-------|--------|------------|------------|---------------------------------------|
| DF   | $1^3B_{1g}^-$ | 1.83   | 0.0        | $|H \rightarrow L + 1\rangle - c.c.(0.5815)$ |
|      |       |        |            |            | $|H - 1 \rightarrow L + 3\rangle - c.c.(0.1207)$ |
| DF   | $1^3A_{g}^+$  | 3.37   | 0.0        | $|H \rightarrow L + 4\rangle + c.c.(0.4773)$ |
|      |       |        |            |            | $|H - 1 \rightarrow L + 2\rangle - c.c.(0.2856)$ |
| I    | $1^3B_{1g}^-$ | 3.47   | 2.208      | $|H \rightarrow L + 1\rangle + c.c.(0.6091)$ |
|      |       |        |            |            | $|H - 1 \rightarrow L + 3\rangle + c.c.(0.0766)$ |
| II   | $1^3A_{g}^-$  | 4.72   | 0.396      | $|H \rightarrow L + 4\rangle - c.c.(0.5163)$ |
|      |       |        |            |            | $|H - 1 \rightarrow L + 2\rangle + c.c.(0.3126)$ |
| III  | $3^3B_{1g}^-$ | 5.51   | 1.816      | $|H \rightarrow L; H \rightarrow L + 2\rangle + c.c.(0.5701)$ |
|      |       |        |            |            | $|H - 1 \rightarrow L; H - 2 \rightarrow L + 1\rangle c.c.(0.1440)$ |
| IV   | $5^3B_{1g}^-$ | 6.78   | 0.743      | $|H \rightarrow L + 1; H - 4 \rightarrow L\rangle - c.c.(0.3970)$ |
|      |       |        |            |            | $|H \rightarrow L + 1; H - 1 \rightarrow L + 2\rangle - c.c.(0.2538)$ |
| V    | $11^3A_{g}^-$ | 7.33   | 0.805      | $|H \rightarrow L; H - 2 \rightarrow L + 2\rangle (0.7543)$ |
|      |       |        |            |            | $|H - 1 \rightarrow L + 7\rangle + c.c.(0.1390)$ |
|      | $12^3A_{g}^-$ | 7.35   | 0.334      | $|H \rightarrow L + 3; H - 1 \rightarrow L + 1\rangle - c.c.(0.3503)$ |
|      |       |        |            |            | $|H \rightarrow L; H - 1 \rightarrow L + 5\rangle - c.c.(0.3135)$ |
Table XII. Excited states contributing to the triplet absorption spectrum of hexacene computed using the MRSDCI method coupled with the standard parameters in the PPP model Hamiltonian. The rest of the information is same as in the caption of Table IV.

| Peak | State   | E (eV) | Transition | dominant contributing configurations |
|------|---------|--------|------------|--------------------------------------|
| DF   | $1^3B_{19}^-$ | 1.67   | 0.0        | $|H \rightarrow L + 1\rangle + c.c.(0.5841)$ |
| DF   | $1^3A_g^+$  | 3.50   | 0.0        | $|H \rightarrow L + 2\rangle + c.c.(0.1239)$ |
| I    | $1^3B_{19}^-$ | 3.57   | 2.153      | $|H \rightarrow L + 1\rangle - c.c.(0.5705)$ |
| I    | $1^3A_g^-$  | 4.61   | 0.218      | $|H \rightarrow L + 3\rangle + c.c.(0.4363)$ |
| II   | $2^3A_g^-$  | 5.15   | 0.647      | $|H \rightarrow L; H \rightarrow L + 1\rangle (0.8093)$ |
| III  | $3^3B_{19}^-$ | 5.62  | 2.119      | $|H \rightarrow L; H \rightarrow L + 3\rangle - c.c.(0.5159)$ |
| IV   | $4^3A_g^-$  | 5.98   | 0.482      | $|H \rightarrow L + 1; H \rightarrow L + 4\rangle c.c.(0.3650)$ |
| IV   | $4^3B_{19}^-$ | 5.98  | 0.380      | $|H \rightarrow L + 1; H \rightarrow L + 3\rangle - c.c.(0.3138)$ |
| V    | $7^3B_{19}^-$ | 6.82  | 1.056      | $|H \rightarrow L + 1; H \rightarrow L + 4\rangle - c.c.(0.4144)$ |
Table XIII. Excited states contributing to the triplet absorption spectrum of hexacene computed using the MRSDCI method coupled with the screened parameters in the PPP model Hamiltonian. The rest of the information is same as in the caption of Table IV.

| Peak | State | E (eV) | Transition | dominant contributing configurations |
|------|-------|--------|------------|--------------------------------------|
| DF   | $1^3B_{1g}^+$ | 1.60   | 0.0        | $|H \rightarrow L + 1\rangle + c.c.(0.5799)$ |
|      |        |        |            | $|H - 1 \rightarrow L + 2\rangle + c.c.(0.1197)$ |
|      | $1^3A_g^+$ | 3.10   | 0.0        | $|H \rightarrow L + 4\rangle + c.c.(0.4573)$ |
|      |        |        |            | $|H - 1 \rightarrow L + 3\rangle + c.c.(0.2732)$ |
| I    | $1^3B_{1g}^-$ | 3.18   | 2.485      | $|H \rightarrow L + 1\rangle - c.c.(0.6018)$ |
|      |        |        |            | $|H - 1 \rightarrow L + 2\rangle - c.c.(0.0854)$ |
|      | $1^3A_g^-$ | 4.50   | 0.191      | $|H \rightarrow L; H - 1 \rightarrow L + 1\rangle (0.6134)$ |
|      |        |        |            | $|H \rightarrow L; H \rightarrow L + 2\rangle + c.c.(0.3260)$ |
| II   | $2^3A_g^-$ | 4.85   | 0.715      | $|H \rightarrow L; H - 1 \rightarrow L + 1\rangle (0.5609)$ |
|      |        |        |            | $|H \rightarrow L + 4\rangle - c.c.(0.3636)$ |
|      | $2^3B_{1g}^-$ | 4.88  | 0.435      | $|H \rightarrow L + 5\rangle + c.c.(0.5435)$ |
|      |        |        |            | $|H - 2 \rightarrow L + 1\rangle - c.c.(0.2464)$ |
| III  | $4^3B_{1g}^-$ | 5.17   | 1.776      | $|H \rightarrow L; H \rightarrow L + 3\rangle - c.c.(0.5398)$ |
|      |        |        |            | $|H - 2 \rightarrow L + 1\rangle - c.c.(0.1420)$ |
| IV   | $5^3B_{1g}^-$ | 6.23   | 1.114      | $|H \rightarrow L; H \rightarrow L + 3\rangle - c.c.(0.5398)$ |
|      | $5^3A_g^-$ | 6.26   | 0.139      | $|H \rightarrow L - 2 \rightarrow L + 1\rangle - c.c.(0.3769)$ |
|      |        |        |            | $|H \rightarrow L + 1; H - 2 \rightarrow L + 1\rangle - c.c.(0.3675)$ |
| V    | $10^3A_g^-$ | 6.77   | 0.159      | $|H \rightarrow L + 2; H - 1 \rightarrow L + 1\rangle - c.c.(0.4111)$ |
|      | $11^3B_{1g}^-$ | 6.85 | 0.441      | $|H \rightarrow L + 2\rangle - c.c.(0.2945)$ |
|      |        |        |            | $|H \rightarrow L; H \rightarrow L + 7\rangle + c.c.(0.2565)$ |
|      |        |        |            | $|H - 2 \rightarrow L + 2\rangle + c.c.(0.2555)$ |
Table XIV. Excited states contributing to the triplet absorption spectrum of heptacene computed using the MRSDCI method coupled with the standard parameters in the PPP model Hamiltonian. The rest of the information is same as in the caption of Table IV.

| Peak | State | E (eV) | Transition Dipole (Å) | dominant contributing configurations |
|------|-------|--------|----------------------|-------------------------------------|
| DF   | $1^3 B_{1g}^+$ | 1.42   | 0                    | $|H \rightarrow L + 1\rangle$ + c.c.(0.5809) |
|      |       |        |                      | $|H \rightarrow L + 4\rangle$ + c.c.(0.1313) |
| DF   | $1^3 A_g^+$   | 3.07   | 0                    | $|H \rightarrow L; H - 1 \rightarrow L + 1\rangle$ (0.4476) |
|      |       |        |                      | $|H \rightarrow L + 5\rangle$ - c.c.(0.2726) |
| I    | $1^3 B_{1g}^-$ | 3.31   | 2.411                | $|H \rightarrow L + 1\rangle$ - c.c.(0.5652) |
|      |       |        |                      | $|H - 1 \rightarrow L + 2\rangle$ - c.c.(0.1612) |
|      | $1^3 A_g^-$  | 4.45   | 0.438                | $|H \rightarrow L; H - 1 \rightarrow L + 1\rangle$ (0.6770) |
|      |       |        |                      | $|H \rightarrow L + 5\rangle$ + c.c.(0.2778) |
|      | $2^3 A_g^-$  | 4.58   | 0.627                | $|H \rightarrow L; H - 1 \rightarrow L + 1\rangle$ (0.5450) |
|      |       |        |                      | $|H - 1 \rightarrow L + 3\rangle$ - c.c.(0.3565) |
| III  | $3^3 B_{1g}^-$| 5.46   | 2.368                | $|H \rightarrow L; H \rightarrow L + 3\rangle$ - c.c.(0.5201) |
|      |       |        |                      | $|H \rightarrow L + 1; H - 5 \rightarrow L\rangle$ c.c.(0.1864) |
| IV   | $9^3 A_g^-$  | 6.48   | 0.314                | $|H \rightarrow L + 2; H - 1 \rightarrow L + 1\rangle$ - c.c.(0.3296) |
|      |       |        |                      | $|H \rightarrow L; H - 1 \rightarrow L + 4\rangle$ - c.c.(0.2959) |
|      | $6^3 B_{1g}^-$| 6.51  | 1.142                | $|H \rightarrow L + 1; H - 5 \rightarrow L\rangle$ c.c.(0.4693) |
|      |       |        |                      | $|H \rightarrow L + 1; H - 1 \rightarrow L + 3\rangle$ c.c.(0.3070) |
Table XV. Excited states contributing to the triplet absorption spectrum of heptacene computed using the MRSDCI method coupled with the screened parameters in the PPP model Hamiltonian. The rest of the information is same as in the caption of Table IV.

| Peak | State | E (eV) | Transition Dipole (Å) | dominant contributing configurations |
|------|-------|--------|----------------------|-------------------------------------|
| DF   | $1^3B_{1g}^-$   | 1.30   | 0.0                  | $| H \rightarrow L + 1 \rangle + c.c.(0.5728)$ |
| DF   | $1^3A_g^+$   | 2.59   | 0.0                  | $| H \rightarrow L + 2 \rangle + c.c.(0.1278)$ |
|      |              |        |                      | $| H \rightarrow L; H - 1 \rightarrow L + 1 \rangle (0.7028)$ |
|      |              |        |                      | $| H \rightarrow L + 2; H - 1 \rightarrow L + 1 \rangle - c.c.(0.2562)$ |
| I    | $1^3B_{1g}^+$ | 2.83   | 2.708                | $| H \rightarrow L + 1 \rangle - c.c.(0.5973)$ |
|      |              |        |                      | $| H - 1 \rightarrow L + 2 \rangle - c.c.(0.0932)$ |
| II   | $1^3A_g^-$   | 3.84   | 0.756                | $| H \rightarrow L; H - 1 \rightarrow L + 1 \rangle (0.8354)$ |
|      |              |        |                      | $| H \rightarrow L + 2; H - 1 \rightarrow L + 1 \rangle - c.c.(0.1082)$ |
| III  | $2^3A_g^-$   | 4.28   | 0.157                | $| H \rightarrow L; H - 1 \rightarrow L + 1 \rangle (0.7992)$ |
|      |              |        |                      | $| H - 1 \rightarrow L + 1; H - 2 \rightarrow L \rangle c.c.(0.1401)$ |
|      | $2^3B_{1g}^-$ | 4.28   | 0.624                | $| H \rightarrow L + 4 \rangle + c.c.(0.4639)$ |
|      |              |        |                      | $| H - 1 \rightarrow L + 2 \rangle - c.c.(3.640)$ |
| IV   | $3^3A_g^-$   | 4.49   | 0.614                | $| H \rightarrow L + 5 \rangle + c.c.(0.5809)$ |
|      | $3^3B_{1g}^-$ | 4.45   | 0.519                | $| H - 1 \rightarrow L; H - 1 \rightarrow L + 1 \rangle (0.1796)$ |
|      |              |        |                      | $| H - 1 \rightarrow L + 2 \rangle - c.c.(0.4166)$ |
|      |              |        |                      | $| H \rightarrow L + 4 \rangle + c.c.(3.838)$ |
| V    | $4^3B_{1g}^-$ | 4.8    | 2.177                | $| H \rightarrow L; H \rightarrow L + 3 \rangle - c.c.(0.5665)$ |
|      |              |        |                      | $| H \rightarrow L + 1; H - 1 \rightarrow L + 3 \rangle c.c.(0.1631)$ |
| VI   | $5^3B_{1g}^-$ | 5.63   | 1.361                | $| H \rightarrow L + 1; H - 5 \rightarrow L \rangle - c.c.(0.5143)$ |
|      |              |        |                      | $| H \rightarrow L + 1; H - 1 \rightarrow L + 3 \rangle - c.c.(0.2377)$ |
| VII  | $8^3B_{1g}^-$ | 6.11   | 0.508                | $| H - 2 \rightarrow L + 4 \rangle + c.c.(0.3988)$ |
|      | $11^3A_g^-$  | 6.17   | 0.299                | $| H \rightarrow L + 1; H - 5 \rightarrow L \rangle - c.c.(0.3343)$ |
|      |              |        |                      | $| H \rightarrow L; H - 1 \rightarrow L + 4 \rangle - c.c.(0.3075)$ |
|      |              |        |                      | $| H \rightarrow L + 2; H - 1 \rightarrow L + 1 \rangle - c.c.(0.3065)$ |
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