Ground and excited state nonlinear optical properties of Poly(-para phenylene vinylene)

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We investigate theoretically the nature of higher energy excited *even* as well as *odd* parity states, for various sizes of oligomers of PPV. We study in detail various nonlinear optical properties, like third harmonic generation (THG), two photon absorption (TPA), electro absorption (EA) of oligomers of PPV within a rigid band correlated Pariser-Parr-Pople (PPP) model Hamiltonian, using the π-electron basis and the powerful multireference single and double configuration interaction (MRSDCI) method. We also use single-double-triple-quadruple configuration interaction (SDTQCI) in limited cases. We show that in THG three kinds of one photon states $1B_u$, jB_u and nB_u (where $j < n$) whereas three kinds of even parity states $2\mathrm{A}_g$, mA_g and kA_g appear. The even parity states $2\mathrm{A}_g$, mA_g and kA_g also appear in TPA. While mA_g absorptions appear just after the nB_u, the $2\mathrm{A}_g$ appears immediately after the jB_u absorptions. A detailed analysis of the wavefunctions of higher energy excited states with conjugation length are presented. We show that beyond certain conjugation length that both mA_g and kA_g states mainly involve excitations between the lowest delocalized valance and conductance bands. Our study indicate middle order exciton binding energy. Finally, we theoretically predict that by optically exciting PPV at one wavelength equivalent to the optical gap for a sufficiently long time to perform nonlinear optical measurement, the values of $\chi^{(3)}$ can be enhanced by three orders-of-magnitude.

Keywords: Poly(phenylene vinylene) and derivatives, Models of non-linear phenomena, Many-body and quasiparticle theories.

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I. INTRODUCTION

Understanding photophysics of phenyl based π-conjugated polymers is essential from fundamental physics as well as application point of view. Phenyl based π-conjugated polymers like poly(-para phenylene vinylene) act as molecular wire are transport passages for charge carriers in organic electronic devices such as organic transistors [1]. These molecular wires include phenylene units which posses nature of ordinary semiconductors and has energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of 2 to 4 eV [2, 3]. The phenylene unit with a benzene ring is a main part of all the molecular electronics and emerging systems like carbon nanotubes etc. Hexagonal lattice in condensed matter is well known to produce flat band which in turn to ferromagnetism [4]. PPV and its derivatives have all pervasive applications in modern technologies, organic light emitting diodes (OLEDS) [5], lasers [6], photovoltaics and photo detectors [7].

Photophysics of PPV and its derivatives are governed by a series of alternating optically allowed one-photon (B_u) and optically opaque two photon (A_g) states. Excitation to any of these classes of states is followed by ultrafast non-radiative decay to the lowest excited state (Internal conversion (IC) [8]). Therefore, fluorescence would usually occur from the lowest excited ($1B_u$) state and its quantum yield is independent of excitation energy — Vavilov-Kasha rule. Below we take note of observations from various experiments [9, 10]. Two prominent bands of different classes of A_g states (mA_g at lower energy and kA_g at higher energies) are identified by various non-linear spectroscopic tools like two photon absorption (TPA), transient photomodulation spectroscopies. Relaxation dynamics of these higher energy even parity states are closely monitored experimentally [9, 10]. It was concluded that while the low energy two photon state (mA_g) that is reached by photoinduced absorption (PA) relaxes to the optical exciton by IC (as its time scale is < 250 fs) whereas the higher energy two photon allowed state (kA_g) decays (only partially) very slowly and possibly dissociates into polaron pairs. Other investigations that reveal similar observation in PPV derivatives, polyfluorene, ladder type poly-(paraphenylene) (PPP) [11–14] and its oligomers makes these phenomena universal for phenyl based polymers.

Above experimental observations demand proper theoretical understanding on the accurate nature of higher energy excited states (wave functions). Such an effort was initiated earlier. Presence of these two different classes of two photon states were found by explicit theoretical

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calculations on phenyl based short oligomers [15, 16]. Such different relaxation dynamics was attributed to their specific electronic nature — mA_g states are superpositions of one electron-hole and two electron-hole excitations between the highest-delocalized valence-band and the lowest delocalized conduction-band states, but the kA_g states have *different* two electron-hole contributions involving both delocalized and localized orbitals. In this work one of our main aims is to present systematically conjugation length dependent nature of various even and odd parity states of PPV that contribute to non-linear optics of these systems. In particular we show that the above mentioned nature of even and odd parity states are valid upto certain conjugation length of the oligomers namely 5-PPV units (PPV5). Beyond PPV5 both the mA_g and kA_g states consist only excitations among various low energy delocalized bands, both one particle-hole and/or two particle holes. In addition some of the kA_g states have one electron-hole excitations among low energy delocalized and localized orbitals. Having investigated the nature of even and odd parity states, it is worthwhile to obtain dipole transitions among these states (which allows one to study various optical properties). Various non-linear optical properties like third harmonic generation (THG), two photon absorption (TPA), electroabsorption (EA) properties of PPV oligomers are presented. Some of our remarkable results are; the energy of the optical state for the largest system size studied is very close to the experimental one, exciton binding energies fall in the moderate range. These calculations indicate existence of 'Kasha' states. Apart from the physics of nonlinear optics, from application point of view, choice of large optical non-linear medium depends not only on the ground state but also excited state matter [17]. Having calculated *ground state* non-linear optical properties and comparing them with available experimental and other theoretical data, we show that *excited state* above mentioned non-linear optical properties can be enhanced by more than two orders of magnitude in the lower frequency region. PPV being strongly photoluminiscent material the first excited one-photon state is below the two-photon state. Therefore, the *excited state* non-linear optical properties are computed from the optical state of real excitations. These findings are also in agreement with earlier experimental and theoretical works (see section V for details).

Rest of the paper is organized as follows. Treating longer range electron correlation in larger molecules is a well known difficulty. In section II we describe in detail about our theoretical model suitable for PPV and detailed method for computation from small to larger oligomer lengths emphasizing on the fact that the transitions among the higher energy delocalized bands are not so important in determining the correlated wave functions (Frozen-d_3 orbital basis state approximation). As utility of the above mentioned approximations Section III describes results obtained for various non-linear optical properties from the ground state and their physical implications. In the section IV we discuss about the nature of excited state even and odd parity wave functions for various conjugation lengths, exciton binding energy, existence of Kasha states etc. In section V we argue that the determination of non-linear optical medium not only depends on the ground state but excited state matter too. We show, excited state nonlinear optical properties could be more than two orders of magnitude larger in the very low frequency range. This agrees well with other experimental and theoretical predictions establishing the validity of the frozen-d_3 orbital basis state approximation. A brief explanation as to why such enhancement can occur and that these results may be experimentally verified for PPV are also provided. In section VI we summarize and discuss our results.

II. THEORETICAL MODEL AND METHODS

Electron correlations have a strong influence on the bonding properties of atoms, semiconductor band gaps [18] as well as photoluminescencece properties [19]. There are a number of studies describing the influence of short as well as long range coulomb interactions [20] in π-conjugated networks. We therefore study various oligomers of PPV within a rigid band correlated π-electron model like Pariser-Parr-Pople (P-P-P) model Hamiltonian,

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

where $\langle ij\rangle$ implies nearest neighbors, $c^{\dagger}_{i\sigma}$ creates an electron of spin σ on the p_z orbital of carbon atom i, $n_{i\sigma} = c^{\dagger}_{i\sigma}c_{i\sigma}$ is the number of electrons with spin σ, and $n_i = \sum_{\sigma} n_{i\sigma}$ is the total number of electrons on atom i. The parameters U and V_{ij} are the on–site and long–range Coulomb repulsions respectively, while t_{ij} is the nearest neighbor one-electron hopping matrix element that includes bond alternation and connectivity. The parameterization of the intersite Coulomb interactions is done in a manner similar to the Ohno parameterization [21]

$$V_{i,j} = U/\kappa(1 + 0.6117R^2_{i,j})^{1/2}\ , \quad (2)$$

where κ is a parameter which has been introduced to account for the possible screening of the Coulomb interactions in the system [22–26]. We have examined both the standard Ohno parameters (U = 11.13 eV, κ = 1.0), as well as a particular combination of U and κ (U = 8.0 eV, κ = 2.0) that was shown previously to be satisfactory at a semiquantitative level for explaining the full wavelength dependent ground state absorption spectrum of PPV [23–25, 27]. We shall use this second set of parameters (U = 8.0 eV, κ = 2.0) in this work. As far as the hopping matrix elements are concerned, we took

$t = -2.4$ eV for the C – C bond in benzene rings. For the vinylene linkage of the PPV oligomers, we chose the hopping elements to be -2.2 eV for the single bond and -2.6 eV for the double bond. We considered PPV oligomers in their planar configurations with the conjugation direction along the x axis. Thus the symmetry group of PPV oligomers is C_{2h}. Since symmetry groups have inversion as a symmetry element, the many electron states of these oligomers can be classified according to this symmetry. The two-photon states of the PPV oligomers belong to the A_g irreducible representation (irrep) of the respective symmetry group, while the one-photon states belong to the B_u irrep. In all the many-body calculations presented in this work, full use of the stated point group symmetries was made.

The correlated electron calculations were performed using the MRSDCI approach, which is a powerful CI technique [28] that has been used previously for linear chain polyenes by Tavan and Schulten [29] as well as by others [30], and by us to calculate the energy crossovers of $2A_g$-$1B_u$ states in polyphenyl- and polydiphenylacetylenes [31]. The methodology behind the MRSDCI calculations is as follows. The calculations are initiated with a restricted Hartree-Fock (RHF) computation of the ground state of the oligomer concerned, followed by a transformation of the Hamiltonian from the site representation (Eq. 1) to the HF molecular-orbital representation. Subsequently, a singles-doubles CI (SDCI) calculation is performed, the different excited states in A_g and B_u subspaces are examined and the N_{ref} configuration state functions (CSFs) making significant contributions to their many-particle wave functions are identified. The next step is the MRSDCI calculation for which the reference space consists of the N_{ref} CSFs identified in the previous step and the overall Hamiltonian matrix now includes configurations that are singly and doubly excited with respect to these reference CSFs (thereby including the dominant triply and quadruply excited configurations). This will be appreciable from the results of Figure 3 discussed later. The new ground and excited states are now re-examined to identify new CSFs contributing significantly to them so as to augment the reference space for the next set of MRSDCI calculations. This procedure is repeated until satisfactory convergences in the excitation energies of the relevant states are achieved. Naturally, this leads to very large CI matrices.

Calculations for smaller number of oligomers of PPV are performed by using full π-electron basis set whereas a slightly different method without loss of generality for longer oligomers is adopted as described below. In Figure 2 we show the free electron electronic energy lables of the three unit PPV (cf. figure caption 2 also) with their characters specified at the right hand side of a label. The PPV3 oligomer contains 22 π-electrons (and hence 22 energy levels, 11 occupied and 11 unoccupied, denoted by $\star$ characters). Corresponding band structure of PPV polymer is shown in Fig. 1 of the ref. [24]. Half of the most interior (exterior) delocalized d (d*) orbitals numbered 1,2,3 (20,21,22) form the d_3 (d_3^*) band of PPV (see Fig. 1 of the ref. [24]), next few interior (exterior) delocalized d (d*) orbitals numbered 4,5,6 (17,18,19) form the d_2 (d_2^*) band whereas the delocalized levels closed to the Fermi level *e.g.*, 10,11 (12,13) form d_1 (d_1^*) bands, in contrast the degenerate localized levels numbered 7,8,9 (14,15,16) form the localized band (cf. Fig. 1 of [24]). In general, a PPVn oligomer will thus contain 8n-2 electrons and (n-1) d_1 (d_1^*) levels, n d_2 (d_2^*) lables and n localized levels corresponding to n benzene rings. We shall show in the later section that these d_3 orbitals do not play any significant role as far as non-linear optical properties are concerned, specially for the longer oligomers. Based on these observations, we 'Freeze' d_3 orbitals from our basis states and do the MRSDCI as earlier [15]. Taking example of PPV3, when we use basis sets with d_3 orbitals frozen, we denote it as PPV3-FRZ-D3. Therefore, in case of PPV3-FRZ-D3 there will only be sixteen orbitals (three occupied d_3 orbitals and the corresponding d_3^* orbitals frozen) instead of twentytwo in PPV3. In general a PPVn-FRZ-D3 will have 6n -2 (3n-1 occupied and 3n-1 unoccupied) levels. Thus larger system sizes can be studied. This is absolutely necessary because in case of THG, TPA, EA etc. calculations for longer oligomers one requires dipole moments among all A_g and B_u states. As a result N_{ref} for both A_g and B_u space Hamiltonians become too large to handle and hence the dimension of the Hamiltonian. However, this problem can be overcome by considering only "Essential" states in both A_g and B_u space Hamiltonians (see below). Thus keeping full basis states is very very computer time and space expensive and will show in great detail that 'Freezing' d_3 orbitals *does not* change the nonlinear susceptibilities *qualitatively*.

III. CORRELATED ELECTRON CALCULATION OF NONLINEAR OPTICAL PROPERTIES OF PPV OLIGOMERS

One of the most general compact formula for third order susceptibility is obtained as [32],

$$\chi^{(3)}_{\hat{j}\hat{k}\hat{l}\hat{m}}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) = \frac{1}{\epsilon_0 N}\frac{e^4}{3!\hbar}P\sum_{a,b,c}\frac{\mu^{\hat{j}}_{0b}\mu^{\hat{k}}_{ba}\mu^{\hat{l}}_{ac}\mu^{\hat{m}}_{c0}}{(E_b - i\Gamma_b - \omega_\sigma)(E_a - i\Gamma_a - \omega_2 - \omega_3)(E_c - i\Gamma_c - \omega_3)} \quad (3)$$

where $\omega_\sigma = \omega_1 + \omega_2 + \omega_3$, a and c denote even (two-photon allowed) and odd (one-photon allowed) states respectively, P represents permutations on the sums $(\hat{j},\omega_1)$, $(\hat{k},\omega_2)$, $(\hat{l},\omega_3)$ and $(\hat{m},\omega_\sigma)$. The formal expression for the non-linear susceptibility relevant to THG studies is obtained by considering $\omega_1 = \omega_2 = \omega_3 = \omega$ so that

$\omega_\sigma = 3\omega$,

$$\chi^{(3)}_{THG}(-3\omega;\omega,\omega,\omega) = \frac{1}{\epsilon_0 N}\frac{e^4}{3!\hbar}$$
$$\sum_{a,b,c}\frac{\mu^{\hat{j}}_{0b}\mu^{\hat{k}}_{ba}\mu^{\hat{l}}_{ac}\mu^{\hat{m}}_{c0}}{(E_b - i\Gamma_b - 3\omega)(E_a - i\Gamma_a - 2\omega)(E_c - i\Gamma_c - \omega)}. \quad (4)$$

Similarly, the formal expression for the non-linear susceptibility relevant to TPA studies can be obtained by setting $\omega_1 = -\omega$ and $\omega_2 = \omega_3 = \omega$ as,

$$\chi^{(3)}_{TPA}(-\omega;-\omega,\omega,\omega) = \frac{1}{\epsilon_0 N}\frac{e^4}{3!\hbar}$$
$$\sum_{a,b,c}\frac{\mu^{\hat{j}}_{0b}\mu^{\hat{k}}_{ba}\mu^{\hat{l}}_{ac}\mu^{\hat{m}}_{c0}}{(E_b - i\Gamma_b - \omega)(E_a - i\Gamma_a - 2\omega)(E_c - i\Gamma_c - \omega)}. \quad (5)$$

We also study non-linear susceptibility relevant to electro absorption (EA), also known as d.c. Kerr effect by setting $\omega_1 = \omega_2 = 0$ and $\omega_3 = \omega$,

$$\chi^{(3)}_{EA}(-\omega;0,0,\omega) = \frac{1}{\epsilon_0 N}\frac{e^4}{3!\hbar}$$
$$\sum_{a,b,c}\frac{\mu^{\hat{j}}_{0b}\mu^{\hat{k}}_{ba}\mu^{\hat{l}}_{ac}\mu^{\hat{m}}_{c0}}{(E_b - i\Gamma_b - \omega)(E_a - i\Gamma_a - \omega)(E_c - i\Gamma_c - \omega)}. \quad (6)$$

In these equations following notations have been used $|0> \equiv 1A_g$ the ground state, $E_b \equiv \omega_{jB}$ energies of odd parity (B_u) states, $E_a \equiv \omega_{kA}$ energies of even parity (A_g) states, $E_c \equiv \omega_{lB}$ energies of odd parity (B_u) states, so that the summing indices a, b, c can be replaced by j,k,l as below

$$\sum_{j,k,l} < 1A_g|\mu|jB_u >< jB_u|\mu|kA_g >< kA_g|\mu|lB_u >$$
$$\times < lB_u|\mu|1A_g > . \quad (7)$$

The triple sum in third order susceptibilities *e.g.*, $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ is over all possible A_g and B_u states and all the energies are with respect to the ground state, $1A_g$. All these eigenstates and energies are obtained by various CI methods as discussed above and the correlated many body wave functions are used to find dipole moments between various odd and even parity states. These dipole moments are used into the sum-over-states formula of Orr and Ward [33] to the desired $\chi^{(3)}$ (Eqns 4 - 6 are representatives). We computed the susceptibility for all photons polarized along the chain as well as in the transverse directions. We present here only the longitudinal component of $\chi^{(3)}_{xxxx}$ s.

Magnitude of $\chi^{(3)}_{xxxx}(-3\omega;\omega,\omega,\omega)$ in arbitrary units is ploted as a function of photon energy in Fig. 3. A line width parameter $\Gamma = 0.05$ eV has been used through out unless specified otherwise. Fig. 3(a) is the result for PPV3 keeping all orbitals (*i.e.*, using full π-electron basis set) and using MRSDCI method, whereas Fig.3 (b) and 3(c) represents that for PPV3-FRZ-D3 using QCI and MRSDCI methods respectively. A few primary observations may be made from Fig.3. First, accuracy of the QCI method is well known and by a closure look at Fig. 3 (b),(c) it is easily appreciable that MRSDCI method is as good as (or better than) QCI because there is *no qualitative difference* between these two figures. Second, d_3 orbitals *do not* play any significant role as far as THG spectrum is concerned. Because, all the figures in Fig.3 are *qualitatively very similar* in terms of the nature of excitons causing the peak and its location. The only difference from the full π electron basis calculation *i.e.*, Fig 3(a) with frozen d_3 basis set calculation is in the higher energy side — there is only a bit of loss of intensity for the higher energy features at the cost of a new feature appearing. It may be noted from earlier studies (cf. Table 1 in [16]) that excitons involving d_3 orbitals were found only in the kA_g state and that too its contribution is very small (for higher oligomers than PPV4 this contribution is negligible, see below). Therefore one can safely use this kind of frozen basis set without any loss of generality so that higher oligomer lengths can be studied with such a powerful technique. We shall show later that 'Frozen-d_3' basis set together with 'essential state mechanism' is most convenient computationally and accurate for PPV and similar materials.

The Figure 3 has five distinct features marked by I, II (and IIa) are attributed to $1B_u$, jB_u whereas III as nB_u respectively and IIIa, IIIb represents mA_g. The odd parity states appear for three photon resonance whereas the even parity states corresponding to two photon resonance. Signature of the $2A_g$ state is seen in between the jA_g and nB_u state. In Fig. 3 (c) we experimented with larger numbers of excited states in each A_g and B_u subspaces. There are only marginal differences between the two, except a little quantitative changes in some of the peak intensities. Thus we shall calculate 50 excited states in each subspaces A_g and B_u and calculate $50 \times 50 = 2500$ dipolemoments among them to calculate various non-linear optical properties to the rest of the paper. A very small peak intensity corresponding to kA_g is seen in Fig. 3 (c) featured as IV.

We continue similar exercises in case of PPV4, PPV5 to convince that the THG spectra obtained using frozen-d_3 orbital approach with large number of excitations included in A_g and B_u subspaces results almost identical to that of full π-electron basis sets. Qualitative nature of the THG spectrum for PPV4, PPV5 are displayed in Figs. 4, 5 respectively. Orders of appearances of various absorption peaks are same as that described earlier in case of PPV3 except that the signatures of $2A_g$ and kA_g peak intensities are enhanced. In case of Fig.s (c) of 3, 4, 5 only essential states are considered. 'Essential state mechanism' was introduced earlier by Guo *et al.* [22] for linear chain PDA systems. In case of PDA only four essential states were required to describe THG property namely, 1A$_g$, mA$_g$, 1B$_u$, nB$_u$. In 'Essential State mechanism' the A_g and B_u space Hamiltonians are constructed only by considering CSFs of relevant states. For example,

the A_g space Hamiltonian for PPV will comprise of relevant CSFs of $1A_g$, $2A_g$, mA_g and kA_g states whereas the B_u space will contain that of $1B_u$, jB_u and nB_u states. (Thus we have $2A_g$, jB_u, kA_g states also as essential states in contrast to earlier studies in PDA [22].) This reduces dimensions of the Hamiltonian greatly and makes it possible to include all CSFs with any significant coefficients, therefore computationally much more efficient. Thus in case of PPV6, PPV7 we actually present results of PPV6-FRZ-d3, PPV7-FRZ-d3 using 'Essential state mechanism' only.

From PPV5 to PPV7 intensities of various peaks are enhanced so much in comparison to others that the kA_g peak is almost not observable in case of PPV7. In case of PPV7, higher energy part of the kA_g absorption band is separately shown in Fig 8. Intensities due to absorption of the jB_u states are enhanced the most in case of PPV7. However, orderings of various peaks $1B_u$, jB_u, $2A_g$, nB_u, mA_g, kA_g remains unaltered. Signature of the $2A_g$ state appears immediately after jB_u (which is absent in case of PDA, as it is non-photoluminiscent material) whereas the m(k)A_g states appear after the nB_u state.

It is worth while to compare other non-linear optical properties like TPA, EA (shown in figures Fig. 9, 10) for PPV. Since TPA process involves absorptions relevant only for two-photon resonant states, a comparison of the same with THG data would help in understanding locations of two- as well as three-photon resonant states in THG spectra. We have discussed THG intensities in detail from PPV3 to PPV7. So for brevity we shall present TPA (as well as EA) data only for the highest oligomer length studied, PPV7. Our calculated TPA, EA resembles well with other theoretical calculations [34]. Although that is a highly approximated calculation but as we show that in larger oligomer limits higher energy excited states involve dominantly excitations involving only d_1 electrons, thus the present calculation shows similarity with the approximated one [34].

We shall discuss about nature of various excited A_g and B_u states as a function of oligomer lengths in the next section. We also comment on the exciton binding energy (which is very controversial) that comes out from this detailed calculations.

IV. NATURE OF EVEN AND ODD PARITY EXCITED STATES

In this subsection we discuss in details the nature of (correlated wave functions) of various even and odd parity excited states in detail. We conclude there are significant changes in the nature of electronic wavefunctions with conjugation lengths, not studied so far in so much details. This is accomplished by describing correlated wave functions from PPV5 to PPV7 in details. We show that till PPV5, description of mA_g and kA_g states according to our earlier results [15] remain valid but beyond PPV5 it is different. The higher excited even and odd parity states may be written as,

$$|xA_g> = \sum_i a_i|d_1 \rightarrow d_1^*>_i + \sum_j b_j|(d_1 \rightarrow d_1^*)^2>_j + \sum_k c_k|d_1 \rightarrow l^*>_k + \sum_k d_k|(d_1 \rightarrow l^*)^2>_l + \sum_m e_k|d_1 \rightarrow d_2^*>_m + \sum_n g_k|(d_1 \rightarrow d_2^*)^2>_n + ...(8)$$

where xA$_g$ is an arbitrary A$_g$ state and each term on the right-hand side contains all even parity CSF's of a given class (for example, $|d_1 \rightarrow d_1^*>_i$ is the i-th even parity configuration of the type $d_1 \rightarrow d_1^*$ whose coefficient in xA$_g$ is a_i etc.). The right hand side of Eqn (8) is obviously not complete and the ... implies existence of many more types of excitations. Once terms have been collected in the above mentioned manner it is possible to quantify the overall contribution of excitations of a given kind (for example, $\sum_i |a_i|^2$ is the total contribution by excitations of the type $d_1 \rightarrow d_1^*$). In tables below we have tabulated contributions from each kind of excitations in various wavefunctions. A close look at the A$_g$ wave functions would indicate clear demarkation in the nature of wave functions, *the (m)kA_g wave functions involve predominantly delocalized $d_{1(2)}$ orbitals* for PPV7. Beyond PPV5 the mA_g states do not have any contribution from delocalized-localized excitations, whereas the states that contribute *weakly* (see also table captions) to the kA_g has one electron-hole (1e-1h) contribution from the delocalized-localized excitations. These kinds of excitations are well known as charge transfer type and are responsible for photo current as well as charge separation phenomena [11, 35]. However, only those wave functions of kA_g which has considerably small dipole coupling to $1B_u$ has contribution from delocalized-localized excitations. Thus there is a conjugation length dependent change in the nature of (m)kA_g states. A look at the tables I,II,III would convince further. Unlike A$_g$ states we do not tabulate various contributions of the coefficients (of eqn(8)) for j(n)B$_u$ states restricting the number of tables. Briefly there natures are as follows. In the smaller chain lengths, j(n)B$_u$ states are predominantly (1e-1h) excitations among the $d_1 \rightarrow d_1^*$ orbitals. The nB_u has substantial (2e-2h) contribution among $d_1 \rightarrow d_1^*$ orbitals as well, along with (1e-1h) $d_1 \rightarrow d_2^*$ excitations. With increasing number of oligomers, $d_1 \rightarrow l^*$ contribution increases in (1e-1h) chanel for jB_u whereas in both chanels of (1e-1h) and (2e-2h) in case of nB_u.

It is worth mentioning at this point that the optical gap decreases with increasing oligomer length and incase of PPV7 the optical gap is 2.3 eV that compares excellently with experimental value of 2.2 eV [9, 10]. This might also shed significant light on the exciton binding energy of PPV which is quite controversial (see for example for binding energy below 0.4 eV [36], moderately higher binding energy from 0.4 to 0.8 eV [37] and for larger binding energy (∼1.0 eV) [38]) *e.g.,* using exciton binding energy E_b = E (conduction band edge) - E (nB_u)

a close look at the Fig 7. yields $E_b = 0.577$ eV where E (nB_u) is taken as the peaked position of nB_u in Fig. 7. Determination of E_b earlier using same method as above yielded larger exciton binding energy [24] because only single configuration interaction (SCI) method was used which does not take care of the many body interactions appropriately.

We would also like to make a mention of the fact that there exists strong dipole coupling between the jB_u to the kA_g states which is stronger than that between 1B_u and kA_g. The jB_u states are inturn strongly coupled to some optically silent A_g states (OSA_g) [39] which are different from 2A_g. Nature of OSA_g states are shown in Fig. 11. These OSA_g states extend from slightly below 2A_g to below mA_g states. These states are not (or weakly) coupled to the 1B_u states. Furthermore there are large numbers of jB_u states (a look at Figs. 6, 7 would indicate the same). We compare in tables IV, V the dipole couplings of kA_g and jB_u states with others like OSA_g states. These OSA_g states are Kasha states.

V. EXCITED STATE OPTICAL NON-LINEARITIES

So far we discussed about the ground state optical non-linear processes *e.g,* THG, TPA, EA for various oligomers of PPV. Excited-state enhancement of optical nonlinearities in linear diphenylhexatriene conjugated molecules was experimentally demonstrated first by Rodenberger *et al.*, [40]. 50 to 160 fold increase in third order nonlinearity was also observed in bacteriochlorophylls (see the other reference of [41]). Theoretical studies on linear chain π-conjugated systems were also carried out by Garito group [40] and a similar enhancement factor as ours were predicted. However, there are no studies (theoretical or experimental) yet on excited state non-linearities of PPV and its derivative compounds. In this section we discuss now nonlinear optical properties from an excited PPV. We are primarily interested in nonlinear optical properties from the optical state. So, in a sense, a laser of suitable wavelength keeps the system (PPV) in the optical state for long enough time for nonlinear optical measurements to be carried out. Our results below predicts that two to three orders-of-magnitude enhancement in various nonlinear optical properties are expected when evaluated from the optical state (see Figures 12 13, 14). These predictions are easily verifiable by experiments. A knowledge of the excited state optical non-linearities can be very easily obtained from Eqns (3–7) by assuming 1B_u as the ground state and measuring all the energies with respect to the 1B_u state.

In general, transition energies $\hbar\omega_{bS_1}$ between the spin state S_1 and intermediate virtual one photon b ($b < 50$ in our study) states are all smaller than the transition energies of the S_0 ground state excitation processes. Furthermore, many excited states with large transition dipolemoments are accessible through the populated S_1 state and the S_b excited states. As it is understandable that the smaller transition energies $\hbar\omega_{ba}$ and larger transition dipolemoment of μ_{ab} cause individual excitation process that make up $\chi^{(3)}$ at the S_1 state to be larger than those of $\chi^{(3)}$ at the ground state S_0. In addition, there are two different channels that contribute to the $\chi^{(3)}$, channel 1: $S_0 \rightarrow S_b \rightarrow S_0 \rightarrow S_b \rightarrow S_0$ where S_b is an one photon allowed excited state. This process can make negative contribution to $\chi^{(3)}$. Channel 2 : $S_0 \rightarrow S_b \rightarrow S_a \rightarrow S_b \rightarrow S_0$ where S_a is a two photon allowed excited state. In contrast to $\chi^{(3)}$ at S_0 which is dominantly channel 1 process, $\chi^{(3)}$ at S_1 is composed of a large number of terms that not only individually larger than those of $\chi^{(3)}$ at S_0 but also have a reduced degree of cancellation effect (*i.e*, having same sign between channel 1 and 2 processes).

Recently, it was theoretically predicted for one dimensional Mott-Hubbard insulators that an enhancement in the excited state non-linear optical properties of seven-orders-of-magnitude [42] is possible. Basic reason for such gigantic enhancement in the excited state non-linear optical properties is near degeneracy of one- and two-photon state and strong dipole coupling between them. Excited state non-linear optical properties in PPV may also be enhanced further by making energy difference between 2A_g and 1B_u smaller. This may be achieved by introducing tortional angel between alternate phenyls of PPV [43].

VI. SUMMARY AND DISCUSSIONS

We beleive following aspects has been achieved in this paper. (i) A comprehensive study on non-linear optical (NLO) properties of shorter to longer oligomers of PPV. (ii) A reasonable method for calculating NLO properties including many body effects of large enough PPV polymers has been obtained. (iii) A middle order exciton binding energy is predicted. (iv) Our calculation provides evidence of Kasha states in clean PPV polymers. (v) We predicted upto three orders of magnitude enhancement in the *excited state* optical nonlinearities which are to be experimentally verified. In the rest of this section we describe below as to how these are achieved.

Motivated by the recent experimental observations of photoinduced absorption in phenyl based organic π conjugated polymers [9–12] we have presented correlated theory of non-linear optical properties like, third harmonic generation (THG), two photon absorption (TPA), electro absorption (EA) in oligomers of PPV in this paper. Understanding these experimental observations pose stiff challenges to theoretical studies — theoretical study must be based on long enough oligomers to mimic realistic situation together with accurate many body calculations. This requires enormous computer memory and time, and it was realized [15] that anything more than PPV4 with full π electron basis is very difficult. This calls for an appropriate scheme so that longer oligomer lengths can be studied. In the later part of Section

II we have described the essence of 'Frozen-d_3' orbital scheme. We showed that, 'Frozen-d_3' orbital scheme is good enough when compared the results of the same with full π-electron basis set. This is done in details for PPV3 to PPV5 oligomers for demonstrations and then results of oligomers upto PPV7 are presented. We then showed that the 'Frozen-d_3' orbital scheme with 'Essential state mechanism' is good enough for describing nonlinear optical properties of PPV.

Using full π-electron basis set for shorter oligomers we demonstrated that the difference in two classes of A_g states are due to their difference in electronic nature— mA_g states are superpositions of one electron-hole and two electron-hole excitations between the delocalized valence-band and the delocalized conduction-band states, but the kA_g states *differ* in two electron-hole contributions involving both delocalized and localized orbitals. Contrary to the above here we demonstrate conjugation length dependent nature of m(k)A_g states. Briefly, in the longer chain limit (PPV5 onwards) *all the features* in the THG, TPA etc. involves primarily various excitations among *delocalized orbitals* d_1 *only* (see also Table -II, III) — perhaps this observation makes earlier studies [30, 34] justified where only d_1-d_1^* bands are kept in the basis set.

We studied in detail non-linear optical properties like, third Harmonic Generation (THG), two photon absorption (TPA), electro absorption (EA) (for PA see reference [39]) for oligomers of PPV within a rigid band correlated Pariser-Parr-Pople (PPP) model Hamiltonian. We used π-electron basis set and the powerful multireference single and double configuration interaction (MRSDCI) method. We have specifically shown that this method is as strong as QCI and also use single-double-triple-quadruple configuration interaction (SDTQCI in short QCI) in limited cases for comparision. We show that in THG three kinds of one photon states $1B_u$, jB_u and nB_u (where $j < n$) appear whereas three kinds of even parity states $2A_g$, m(k)A_g appear. We have categorically described all these excitons using the above mentioned many body calculations in Tables I to III. While mA_g absorptions appear just immediately after the nB_u, the $2A_g$ appears immediately after the jB_u absorptions. In obtaining THG spectrum a *low* line width parameter $\Gamma = 0.05eV$ has been used. However, experimental line width parameter could be much larger than this one and one may miss the $2A_g$ feature in THG which appear as shoulder of the jB_u peak (for short oligomers). In literature, Γ values as large as 0.3 eV has been used [24], if such a large Γ value is employed here, one may end up only one broad peak (or possibly two), as is seen in one of the earlier experiments [44]. In case of linear chain materials like polydiaccetylene (PDA) it was shown earlier [22] that $2A_g$ is not an essential state for THG and electroabsorption. However from our calculated THG intensity for PPV6 and PPV7 the feature due to $2A_g$ is quite pronounced enough and possibly detectable in fresh experiments.

While it is well known that PPVs are strongly photoluminescent material but there is huge controversy regarding the nature of light emitted by the excitons, *e.g*, the 'binding energy' of excitons (ranging from 0.1 eV to 1 eV, an order of magnitude, cf. [36–38, 45]), from our calculation we predict exciton binding energy in the middle order (0.57 eV). Finally, one of the important aspects of the present work is prediction of two to three orders of magnitude enhanced *excited state* non-linear optical properties. Earlier theoretical as well as experimental attempts on nonresonant enhancement of third order susceptibilities in some other organic molecules by Garito group [40] showed similar conclusion. Thus our 'frozen-d_3' scheme has been used as testing ground. However, recently it is shown for one dimensional Mott-Hubbard insulators [42] that such enhancement in excited state optical nonlinearities could be as large as seven orders-of-magnitude. Main reason for such gigantic enhancement is occurence of almost energetically degenerate one- and two-photon states with very large dipole coupling between them. We believe similar situation may appear also in case of PPV or related materials. Energy difference between the $1B_u$ and $2A_g$ states and hence dipole coupling between them may be tuned through creating torsional angles between phenyles [43]. It is worth pointing out that while evaluating excited state optical non-linearities same geometric structure as the ground state has been used, which may not be the case and may modify our predictions. This aspect remains to be clarified through future studies.

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FIG. 1: The planar PPV2 oligomer that terminate with benzene molecules at both ends, in order to preserve spatial symmetry.

FIG. 2: Schematic electronic structure of the three unit PPV (PPV3) oligomer in the non-interacting limit. The interior one to six-th orbitals are delocalized orbitals (denoted by d_3, d_2) and the corresponding exterior unoccupied orbitals seventeen to 22nd are denoted by $d_2^\star$, $d_3^\star$ respectively. The intermediate localized three orbitals (l) seven to nine are due to the presence of three benzenes in the oligomer (the corresponding three unoccupied orbitals fourteen to sixteen represented by $l^\star$). Two delocalized orbitals (d_1) closed to the Fermi level (represented schematically by a dashed line) ten, eleven and the corresponding virtual orbitals twelve, thirteen (d_1^*) are most relevant as far as low energy optics is concerned.

FIG. 4: Magnitude of the THG susceptibility in arbritrary units as a function of photon energy for four units of PPV (PPV4) with full π electron basis using MRSDCI method **(a)**. The middle panel **(b)** represents the same as above for frozen-d_3 orbital basis set of PPV4 (PPV4-FRZ-d_3). Whereas **(c)** represents the same as that of **(b)** but with larger number of excited states involved in calculating the intensity. The line width parameter for all these figures is $\Gamma = 0.05$ eV.

FIG. 5: THG intensity for PPV5. The upper panel **(a)** represents the calculated THG for PPV5 using full π-electron basis. The middle panel **(b)** represents the same for the PPV5-FRZ-d3 whereas the **(c)** represents the THG intensity for PPV5-FRZ-d3 with larger (than **(a)** and **(b)**) number of excited states involved. Qualitatively all the figures are equivalent and therefore proves the accuracy of the 'frozen-d_3' orbital approach for PPV. The line width parameter is $\Gamma = 0.05$ eV.

FIG. 6: The THG intensity of PPV6 with frozen-d_3 orbitals. The line width parameter is $\Gamma = 0.05$ eV.

FIG. 7: The THG intensity of PPV7 with frozen d_3 orbitals. Resemblance of all the calculated intensities for PPV3 to PPV7 indicates universal features of PPV polymer.

FIG. 3: Magnitude of the THG susceptibility $|\chi^{(3)}_{xxxx}(-3\omega;\omega,\omega,\omega)|$ in arbitrary units as a function of energy (in eV) for 3 unit PPV oligomer (PPV3). Fig. 3 (a) represents the calculated spectra using MRSDCI method keeping all the orbitals. Fig 3 (b) represents the THG intensity using SDTQCI method and with frozen d_3 orbitals whereas Fig 3 (c) represents the same as in Fig. 3 (b) using MRSDCI method. A line width parameter $\Gamma = 0.05$ eV has been used. All the three figures are qualitatively similar, showing the powerfullness of the MRSDCI technique as well as validity of the Frozen d_3 orbital approach.

FIG. 8: Higher energy part of the THG intensity of PPV7 based on the frozen d_3-π orbital basis set.The intensity of kA_g states is small in Fig. 7 which are shown here.

FIG. 9: The TPA intensity of PPV7 based on the frozen d_3-π orbital basis set. The first peak is the location of 2A_g state, next two peaks correspond to the mA_g state, the higher energy kA_g states are shown pronounced in the inset figure. A comparison of this with Fig. 7 would explain observation of A_g peaks in the THG spectra.

FIG. 10: The EA of PPV7 based on the frozen d_3-π orbital basis set.

FIG. 11: Pictorial presentations of the OSA_g states that do not have double excitations like $2A_g$ state

FIG. 12: The excited state THG intensity of PPV7 with respect to the same calculated from the ground state. Upto three orders of magnitude enhancement in the lower frequency regime is predicted.

FIG. 13: The excited state TPA intensity of PPV7 with respect to the same calculated from the ground state. Two to three orders of magnitude enhancement in the lower frequency regime is predicted.

FIG. 14: The excited state EA intensity of PPV7 with respect to the same calculated from the ground state. Two to three orders of magnitude enhancement in the lower frequency regime is predicted.

TABLE I: Nature of various even parity excited states for PPV5 oligomer. These should be compared with higher oligomers of PPV, namely PPV6, PPV7

State	E(nA_g) eV	$d_1 \rightarrow d_1^*$	$(d_1 \rightarrow d_1^*)^2$	$(d_1 \rightarrow d_2^*)$	$(d_1 \rightarrow l^*)^2$	$d_1 \rightarrow d_3^*$
$2A_g$	3.69	0.58	0.1			
mA_g : $4A_g$	4.25	0.073	0.5			
: $5A_g$		0.56	0.08			
: $6A_g$		0.02	0.07	0.48		
: $7A_g$		0.05	0.40	0.08		
: $8A_g$		0.20	0.28			
kA_g : $11A_g$	5.65	0.034	0.33	0.13		
: $12A_g$		0.024	0.27	0.15	0.08	0.029
: $14A_g$			0.45		0.18	
: $15A_g$		0.068	0.16		0.07	
: $16A_g$			0.012	0.40	0.15	

These CI coefficients are obtained using full π-electron basis. For PPV5-FRZ-d_3 results are almost same.

TABLE II: Nature of various even parity excited states for PPV6 oligomer. These should be compared with higher oligomers of PPV, namely PPV5, PPV7

State	E(nA_g) eV	$d_1 \rightarrow d_1^*$	$(d_1 \rightarrow d_1^*)^2$	$(d_1 \rightarrow d_2^*)$	$(d_1 \rightarrow l^*)$	$(d_1 \rightarrow l^*)^2$
$2A_g$	3.46	0.75	0.05			
mA_g : $5A_g$	4.24	0.82				
: $8A_g$		0.03	0.75			
: $12A_g$		0.88				
: $13A_g$		0.14	0.57			
kA_g : $19A_g$	5.39	0.12	0.61			
: $23A_g$		0.31	0.27	0.027		
: $24A_g$		0.22	0.03	0.34	0.03	
: $26A_g$		0.26	0.014	0.36	0.03	
: $27A_g$			0.23	0.38	0.03	0.02
: *$28A_g$			0.26	0.26	0.24	0.02
: *$29A_g$			0.10	0.01	0.73	
: *$30A_g$		0.01	0.43	0.20	0.045	

*contribution of these states to kA_g is very weak as coupling of these states to the $1B_u$ state is very weak (*e.g.*, corresponding dipole couplings are less than equal to 0.25).

TABLE III: Nature of various even parity excited states for PPV7 oligomer. These should be compared with higher oligomers of PPV, namely PPV5, PPV6

State	E(nA_g) eV	$d_1 \rightarrow d_1^*$	$(d_1 \rightarrow d_1^*)^2$	$(d_1 \rightarrow d_2^*)$	$(d_1 \rightarrow l^*)$	$(d_1 \rightarrow l^*)^2$
$2A_g$	3.40	0.79	0.02			
mA_g:5A$_g$	4.05	0.87				
mA_g:6A$_g$		0.88				
mA_g:7A$_g$			0.75			
mA_g:8A$_g$		0.85				
mA_g:9A$_g$		0.83				
kA_g:11A$_g$	4.75	0.03	0.65			
12A$_g$		0.09	0.70			
*13A$_g$		0.57	0.02	0.16		
*14A$_g$		0.073			0.73	
*15A$_g$		0.46	0.023		0.29	
16A$_g$		0.13	0.46			
*17A$_g$		0.08			0.77	

*contribution of these states to kA_g is very weak as coupling of these states to the 1B$_u$ state is very weak (*e.g.*, corresponding dipole couplings are less than equal to 0.25). The energies of various A$_g$ states obtained from our calculations in tables I, II,III may be compared with other calculations in [30, 34].

TABLE IV: Dipole coupling (x,y components) between one photon $1B_u$, some of the jB_u states with some of the two photon states of kA_g and OSA_g for PPV6. jB_us are very strongly coupled to the kA_g states; jB_us are again strongly dipole-coupled to the OSA_gs– *indicative* of decay of kA_g to OSA_g via jB_us.

jB_u	kA_g	$< jB_u\|\mu\|kA_g >$	jB_u	OSA_g	$< jB_u\|\mu\|OSA_g >$	$< 1B_u\|\mu\|kA_g >$
4	19	1.02,0.21	2	2	3.63,0.62	1.63,0.43
12	19	2.01,0.34	3	2	3.11,0.53	
13	19	1.71,0.32	4	2	1.60,0.34	
15	19	1.94,0.35	5	2	1.11,0.11	
4	23	0.60,0.14	3	4	3.53,0.6	0.87,0.25
12	23	1.32,0.23	12	4	2.33,0.4	
13	23	1.03,0.20	13	4	3.10,0.4	
15	23	1.67,0.29	15	4	2.4,0.45	
7	26	1.38,0.24	2	5	2.29,0.40	0.45,0.14
13	26	1.00,0.14	3	5	1.78,0.3	
14	26	0.78,0.22	7	5	2.37,0.4	
15	26	0.65,0.05	10	5	3.03,0.5	

TABLE V: Dipole coupling (x,y components) between one photon 1B$_u$, some of the jB$_u$ states with some of the two photon states of kA$_g$ and OSA$_g$ for PPV7. jB$_u$s are very strongly coupled to the kA_g states; jB_us are again strongly dipole-coupled OSA_gs– *indicative* of decay of kA_g to OSA_g via jB_us.

jB_u	kA_g	$< jB_u\|\mu\|kA_g >$	jB_u	OSA_g	$< jB_u\|\mu\|OSA_g >$	$< 1B_u\|\mu\|kA_g >$
3	11	1.25,0.21	2	2	3.96,0.69	2.28,0.51
11	11	1.51,0.27	6	2	3.42,0.49	
17	11	0.88,0.17	8	2	2.19,0.37	
8	12	1.32,0.29	2	4	2.31,0.41	1.92,0.49
13	12	0.92,0.17	3	4	2.80,0.48	
17	12	1.15,0.22	10	4	2.81,0.47	
8	16	0.99,0.24	8	5	3.86,0.67	1.11,0.33
12	16	0.70,0.12	11	5	4.46,0.77	
13	16	0.93,0.18	13	5	4.98,0.85	