

Electronic structure analysis and vertical ionization energies of thiophene and ethynylthiophenes

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Abstract. Results from different decouplings of the electron propagator theory using MP2/6-311g (2df, 2p) and MP2/6-311++g (2df, 2p) optimized geometries have been performed to investigate first eight vertical ionization energies and the corresponding Dyson orbitals. The results computed are in good agreement with experimental ionization energies and help clear the ambiguities of experimental photoelectron spectrum (PES) assignments. Detailed examination of the π -orbital density distribution of Dyson orbitals provides clarity in PES assignments and new insights about the topology of ring π and ethynyl π_{c-c} electron density distribution which may be tapped for improved nonlinear optical/electrochemical response from the thiophenic conjugated polymers.

Keywords. Thiophenic conjugated polymers; electron propagator; ionization energy; Dyson orbital, π electron density.

1. Introduction

Conjugated polymers have attracted considerable attention as novel materials due to their potential for many applications in electronics and optoelectronic devices.^{1–13} Among numerous conjugated polymers, the polythiophenes with non-degenerate ground state have received much attention for their use in electrical energy storage in rechargeable batteries,¹⁴ in photovoltaic cells,¹⁵ in nonlinear optical devices,¹⁶ polymer light emitting diodes,¹⁷ electrochemical sensors and modified electrodes¹⁸ etc. The polythiophenes also show a relatively high degree of stability vis-à-vis atmospheric degradation, in ultra-high vacuum and in many organic solvents. Recently, thiophene-containing conjugated polymer bearing ethyne groups and metal centers inserted between thiophene rings have been developed.¹⁹ The spacing of the thiophene rings with the electron-rich acetylide and metal centre moieties should result in the enhancement of both electron density and conjugation and thus delocalization throughout the polymer chain and an understanding of the basic electronic structure of the monomer units can help understand and enhance their utility.

In this paper, we focus on conjugated ethynylthiophenes which have emerged as a suitable model

for the organic spacers.¹⁹ Their electrical conductivity depends on several important electronic structure parameters such as ionization energy, electron affinity and band gap. An earlier attempt at structural understanding from first principles had been made by Novak *et al*²⁰ by recording the ultraviolet Photo-Electron Ionization Spectrum (PES) of two isomeric ethynyl and four isomeric diethynylthiophenes. Due to strong overlap between PES bands they are not sure whether recorded spectrum gives correct adiabatic or vertical ionization energies and attempts to use MO eigenvalues and eigenvectors from semiempirical AM1²¹ and PM3²² methods reported in the same paper has not provided a satisfactory resolution of PES band assignments. The use of more reliable *ab-initio* theoretical techniques to supplement and interpret the photoelectron spectral (PES) data is of obvious importance.

The electron propagator theory^{23–25} has emerged as a computationally economic and accurate method for calculation of vertical ionization energies and provides a framework for the systematic inclusion of electron correlation and orbital relaxation effects in a one-electron picture of molecular structure. The corresponding Dyson orbitals provide electronic structure interpretations that accompany electron attachment and detachment processes.^{26–28} Accurate calculations using other correlated methods even at the level of MP2 will require a separate calculation for the neutral target and each ionized state, with a

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small ionization energy being obtained as a difference between two large total energies. The use of these methods for calculating vertical ionization energies of ethynylthiophenes is therefore computationally more demanding and the results so obtained less satisfactory due to the difference in correlation and relaxation effects between N and $N-1$ electron system even when same primitive basis is used for both. The electron propagator theory provides vertical electron binding energies for ionization from any orbital from a single calculation and permits systematic improvement in incorporation of correlation and relaxation effects.²⁹ For these reasons, the EPT-based methods have emerged as an economic, efficient and reliable tool for direct computation of ionization energies from a single calculation. We have shown previously, that the EPT decouplings provide new insights with accurate resolution of PES for large organic molecules.^{30–32} It is our purpose in this paper to apply various decouplings of the one electron propagator on ethynylthiophenes, using sufficiently large basis sets to provide dependable results which can be utilized for accurate understanding of photoelectron data that are available for this important class of monomers with potential for multifaceted practical applications.

2. Methods

Electron propagator calculations for vertical electron detachment and attachment energies are based on the Dyson equation.^{26,27} The Dyson equation governing all electron propagator decouplings may be rewritten in the form of one-electron equations such that

$$[\hat{f} + \hat{\Sigma}(\varepsilon_i)]\phi_i^{Dyson}(x) = \varepsilon_i\phi_i^{Dyson}(x), \quad (1)$$

where \hat{f} , is the one-electron Hartree–Fock (HF) operator and $\hat{\Sigma}(\varepsilon)$ is an energy-dependent non-local operator, the so-called self-energy.²³ This operator describes electron correlation and orbital relaxation effects that are neglected by the Fock operator, \hat{f} . Eigenfunctions of (1) are the Dyson orbitals, ϕ_i^{Dyson} . For vertical electron detachment processes, the Dyson orbitals are given by

$$\phi_i^{IP,Dyson}(x_N) = \sqrt{N} \int \Psi_N(x_1, x_2, x_3, \dots, x_N) \Psi_{i,N-1}^*(x_1, x_2, x_3, \dots, x_{N-1}) dx_1 dx_2 \dots dx_{N-1}. \quad (2)$$

Here, $\Psi_N(x_1, \dots, x_N)$ is the wavefunction for the N -electron, initial state and $\Psi_{i,N\pm 1}(x_1, \dots, x_{N\pm 1})$ is the wave function for the i -th final state with $N \pm 1$ electrons. In both expressions, x_j represents the space-spin coordinates of electron j . The eigenvalues, ε_i , of the Dyson equation correspond to electron binding energies of the molecular system. By using perturbative arguments, one may justify neglect of off-diagonal matrix elements of the self-energy operator in the HF basis. This leads to the simpler quasi-particle expression, also called the diagonal approximation.^{23,26–28,33,34} Thus, the electron binding energies in the quasi-particle approximation read $\varepsilon_i^{HF} + \sum_{ii}(E) = E$, where ε_i^{HF} is the i -th canonical, HF orbital energy. All EPT methods used in this paper are based on this class of approximation, namely, diagonal second and third order, P3 and OVGf.^{23–25,33–36} The pole strength, P_i , is a good indicator of the qualitative validity of this approximation and is defined as

$$P_i = \int |\phi_i^{Dyson}(x)|^2 dx. \quad (3)$$

The Dyson orbital^{26,27} within the diagonal approximation is simply proportional to a normalized, canonical HF orbital such that

$$\phi_i^{Dyson}(x) = \sqrt{P_i} \psi_i^{HF}(x). \quad (4)$$

Thus, the pole strength takes values between zero and unity. If the ionization process is well described by a Koopmans (frozen-orbital) picture, pole strengths are very close to 1.0. When pole strengths are less than 0.8, non-diagonal analysis of energy poles is required. All pole strengths in this work exceed 0.8.

All computations were performed using the Gaussian03 suite of programs.³⁷ Geometry optimizations and frequency calculations for thiophene and ethynylthiophenes presented here were performed at the MP2 level of theory with 6-311g (2df, 2p) and 6-311++g (2df, 2p) basis set to examine if additional diffuse functions provide superior to treatment of S lone pairs. Geometry optimizations were done using MP2. Thiophene, 2-ethynylthiophene, 3-ethynylthiophene, 2,4-diethynylthiophene and 2,3-diethynylthiophene have Cs Symmetry while 2,5-diethynylthiophene and 3,4-diethynylthiophene have C_{2v} symmetry. The Dyson orbital pictures presented in the Tables were created with GaussView, and an isosurface value of 0.02 was used to produce these figures.

3. Results and discussion

The pressing problem in resolution of structural features of thiophene and its acetyl variants is the ambiguity in assignment of closely spaced ionization peaks which can not be resolved conclusively at the level of Koopmann's Theorem (KT) or using orbital energies from semiempirical variants like AM1 and PM3 used earlier for these systems.²⁰ A dependable assignment of ionization energies and its correlation with orbital topology will facilitate the choice of monomer moiety with greater promise of interaction between the acetyl π_{c-c} and thiophenyl ring π electron densities which can be exploited for calibrated steering of desired nonlinear optical and electrochemical attributes and as stated earlier, our aim here is to assist in this task by presenting EPT results for unambiguous PES assignments and the corresponding Dyson orbitals to isolate σ/π character and extent of π_{c-c} and ring π electron density interaction. Towards this end, we offer a tabulation of EPT poles from various decouplings and corresponding Dyson orbitals from both 6-311g (2df, 2p) and 6-311++g (2df, 2p) basis sets. The results for thiophene are shown in table 1; for further molecules the results are given in supplementary information (tables S1–S6, see www.ias.ac.in/chemsci).

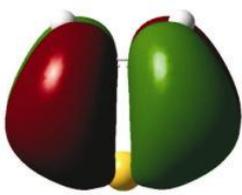
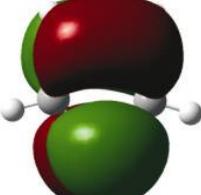
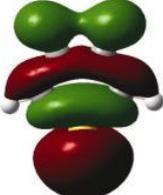
The energetically highest eight orbitals for thiophene, 2-ethynylthiophene, 3-ethynylthiophene, 2,3-diethynylthiophene, 2,3-diethynylthiophene, 2,5-diethynylthiophene and 3,4-diethynylthiophene are seen to be within the experimental PES energy range investigated by Novak *et al.*²⁰ and have been chosen by us for detailed examination. Thiophene, free from any ethyne group, has 3 π and 19 σ type orbitals. Our EPT results and corresponding Dyson orbitals for this system are collected in table 1. Thiophene HOMO, HOMO-1 and HOMO-3 are of π type in which first two have two nodal planes. One nodal plane is the molecular plane and other one is perpendicular to it. However, HOMO-3 has only one nodal plane i.e. the molecular plane. In HOMO, perpendicular plane passes through the middle of C3–C4 and S atom while in HOMO-1 it cuts the molecular plane through C2 and C5. The participation of S atom in HOMO is minimal but significant in HOMO-1 and HOMO-3. Out of 19 σ type Dyson orbitals, the extent of localization of the lone pair orbital density on S-atom is quite large on HOMO-2 which is classified as the n_s orbital.

HOMO-4, HOMO-5, HOMO-6 and HOMO-7 are of σ -type and therefore not of much interest for nonlinear optics/electrochemical attributes of thiophenic conjugated polymer. Furthermore, as can be easily inferred from the results of table 1, the EPT decouplings provide a much superior agreement with experimental ionization data and among these, in keeping with our previous investigations,^{30–32} we will rely on the P3 decoupling for its greater dependability^{35,36} and computational efficiency. P3 results from both the basis sets are within 1 eV of each other even for orbitals with large amplitude on the S-atom and in our discussion, further qualitative/quantitative differentiation between results from these two basis sets will not be attempted. Near total convergence of results from both these disparate primitive basis sets is taken as a positive affirmation of our computed data. The close proximity between the various EPT results and the experimental ionization energies is as expected and that in many cases the EPT corrections to the KT results exceeds 1 eV underscores the need for revisiting these important thiophenic monomers with improved EPT decouplings employed here.

Both 2-ethynylthiophene and 3-ethynylthiophene has 4 π and 24 σ type orbitals. HOMO, HOMO-1, HOMO-3 and HOMO-5 are of π type in which HOMO has three nodal planes. One is the molecular plane and other two are perpendicular to it. HOMO-5 Dyson orbital, having only one molecular nodal plane, has maximum delocalization of electron density between ring and ethyne group whereas zero participation of ethyne group is seen in case of HOMO-1 which has two nodal planes. In HOMO-3, electron density delocalization is divided into two parts i.e. S1–C5–C4 and C2–C6–C7–H8 with no role for C3. As can be seen in supplementary tables S1 and S2, the HOMO-3 orbital for both 2 and 3-ethynylthiophenes is predominantly acetyl π_{c-c} in nature for both the monoethynyl thiophenes.

2,5-Diethynylthiophene, 3,4-diethynylthiophene, 2,3-diethynylthiophene and 2,4-diethynylthiophene have 5 π and 29 σ type orbitals. In all these diethynylthiophenes HOMO, HOMO-1, HOMO-4/HOMO-3, HOMO-5 and HOMO-7 are of π type in which four nodal planes have been found in the first two HOMO/HOMO-1 Dyson orbitals except in HOMO-1 of 2,5-diethynylthiophene which has no contribution from the acetyl π_{c-c} moieties and has only two nodal planes. HOMO-4, HOMO-5 and HOMO-7 of all four diethynylthiophenes have three, two and one

Table 1. Vertical electron detachment energies of thiophene and the corresponding Dyson orbitals.

	HOMO		HOMO-1		HOMO-2		HOMO-3	
								
	A2		B1		A1		B1	
	g2df2p	++g2df2p	g2df2p	++g2df2p	g2df2p	++g2df2p	g2df2p	++g2df2p
KT	8.80	8.85	9.36	9.44	12.89	12.97	14.22	14.29
Second order	8.58	8.62	9.01	9.06	11.51	11.56	12.38	12.42
Third order	8.95	9.03	9.33	9.41	12.32	12.40	13.21	13.29
OVGF	8.84	8.91	9.25	9.33	12.02	12.09	12.88	12.94
P3	9.06	9.12	9.31	9.38	12.02	12.09	12.83	12.90
Experiment (ref 37)	8.87		9.52		12.1		12.7	
	HOMO-4		HOMO-5		HOMO-6		HOMO-7	
								
	B2		A1		B2		A1	
	g2df2p	++g2df2p	g2df2p	++g2df2p	g2df2p	++g2df2p	g2df2p	++g2df2p
KT	14.35	14.45	14.98	15.07	15.55	15.63	18.93	19.01
Second order	12.78	12.83	12.78	12.82	13.43	13.45	16.35	16.38
Third order	13.70	13.79	14.05	14.15	14.53	14.62	17.58	17.67
OVGF	13.30	13.37	13.46	13.53	14.04	14.11	17.09	17.16
P3	13.46	13.53	13.73	13.81	14.21	14.28	17.00	17.13
Experiment (ref 38)	13.3		13.9		14.3		16.6	

nodal planes respectively while HOMO-4 of 2,5-diethynylthiophene is a σ -type Dyson orbital. HOMO, HOMO-1 and HOMO-4 Dyson orbitals of 2,4-diethynylthiophene and HOMO, HOMO-1 Dyson orbitals of 3,4-Diethynylthiophene, 2,3-Diethynylthiophene and 2,5-diethynylthiophene have disjointed density distribution between the ring π and acetyl π_{c-c} . HOMO-4 orbital of all four diethynylthiophenes has large c-c localization on the two ethynyl moieties. In case of 2,5-diethynylthiophene the HOMO-4 has σ character but for other diethynylthiophenes it is of π type with a nodal plane between the two ethynyl π_{c-c} moieties. HOMO-5 orbital of all the four diethynylthiophenes has only one nodal plane with considerable overlap between ring and ethyne group π electron densities. There is strong overlap between the π_{c-c} densities of both ethyne groups for 2,3 and 3,4-diethynylthiophenes while for 2,4 and 2,5-diethynyl-

thiophenes the nodal plane bisects the molecule between two halves with disjointed ethynyl π_{c-c} and ring π electron densities. HOMO-7 of all four diethynylthiophenes has seamless integration of π electron density between the ring and both the ethynyl moieties. The calculated P3 EPT ionization energies in all cases is quite close to experimental values. These features correlate very well with details of energy assignment offered in figure 1, where the differences in our assignment of inner orbitals from those of Novak *et al*²⁰ demonstrate the advantages of the *ab initio* correlated EPT calculations.

4. Concluding remarks

It has been our purpose to explore the energetics and density distribution of π orbitals of thiophene and its mono and di-ethynyl variants to provide unambigu-

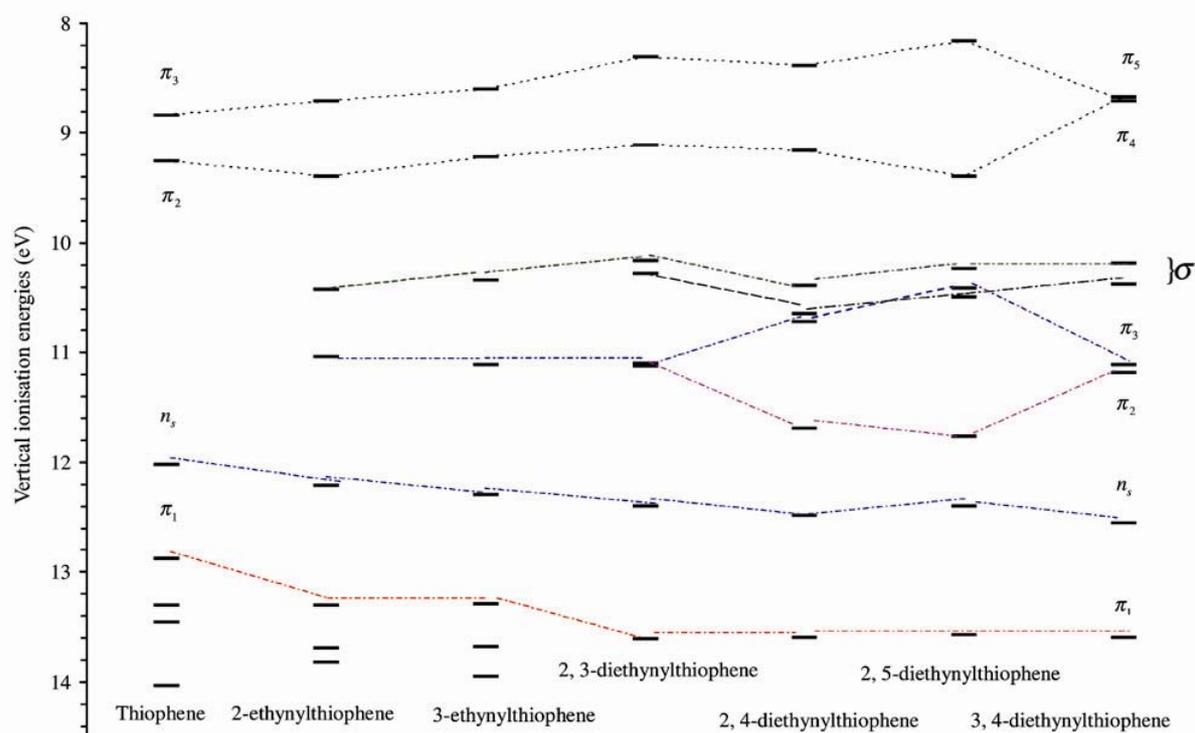


Figure 1. Correlation diagram for ionization energies of thiophenes and ethynylthiophenes.

ous PES assignment and to try and go beyond simple energetics in identifying the monomer(s) with best promise as polymeric materials with high nonlinear optical and electrochemical response.

In terms of simple energetics the bundling of HOMO-2, HOMO-3, HOMO-4 and HOMO-5 in a common π_{c-c} set by Novak *et al.*²⁰ is clearly untenable as shown in figure 1 of this paper. The HOMO-2 and HOMO-3 are σ -type for all diethynylthiophene variants is a pointer to the need for rigorous large basis set *ab initio* correlated techniques employed here. Detailed examination of the π -orbital density distribution of Dyson orbitals presented here also seems to indicate the need for a re-assessment of 2,5-diethynylthiophene as being most promising monomer due to the lowest ionization energy of its π HOMO. As we have shown, the seamless interaction between the ring π and acetyl π_{c-c} electron densities is present only in HOMO-7 π orbital of diethynyl variants and HOMO-5 of mono ethynyl variants. The more loosely bound lower energy π orbitals have a segregation between the ring and acetyl electron densities. Since non linear optical response is based on ease and extent of polarisability, it seems to us that one needs to consider ways of modifying

the HOMO-7/HOMO-5 attributes of diethynyl/monoethynyl thiophenes using appropriate substituents for the H-atom of the ethynyl groups so that we have a monomer where looseness of electron density distribution across the whole molecule is combined with lower binding energies as well. The studies along these lines are underway in our group.

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