



Unraveling the luminescence signatures of chemical defects in polyethylene

Lihua Chen, Huan Doan Tran, Chenchen Wang, and Rampi Ramprasad

Citation: The Journal of Chemical Physics **143**, 124907 (2015); doi: 10.1063/1.4931986 View online: http://dx.doi.org/10.1063/1.4931986 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/143/12?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in

Calculation of longitudinal polarizability and second hyperpolarizability of polyacetylene with the coupled perturbed Hartree-Fock/Kohn-Sham scheme: Where it is shown how finite oligomer chains tend to the infinite periodic polymer

J. Chem. Phys. 136, 114101 (2012); 10.1063/1.3690457

Structure and properties of metal-exchanged zeolites studied using gradient-corrected and hybrid functionals. II. Electronic structure and photoluminescence spectra J. Chem. Phys. **136**, 064502 (2012); 10.1063/1.3676409

Hole localization in [AlO 4] 0 defects in silica materials J. Chem. Phys. **122**, 144704 (2005); 10.1063/1.1880972

Ionic and electronic processes in quartz:Mechanisms of thermoluminescence and optically stimulated luminescence J. Appl. Phys. **92**, 5036 (2002); 10.1063/1.1510951

Self-doping of cadmium stannate in the inverse spinel structure Appl. Phys. Lett. **80**, 1376 (2002); 10.1063/1.1452789









Unraveling the luminescence signatures of chemical defects in polyethylene

Lihua Chen, Huan Doan Tran, Chenchen Wang, and Rampi Ramprasad^{a)} Department of Materials Science and Engineering, Institute of Materials Science, University of Connecticut, 97 North Eagleville Road, Storrs, Connecticut 06269, USA

(Received 17 March 2015; accepted 17 September 2015; published online 30 September 2015)

Chemical defects in polyethylene (PE) can deleteriously downgrade its electrical properties and performance. Although these defects usually leave spectroscopic signatures in terms of characteristic luminescence peaks, it is nontrivial to make unambiguous assignments of the peaks to specific defect types. In this work, we go beyond traditional density functional theory calculations to determine intra-defect state transition and charge recombination process derived emission and absorption energies in PE. By calculating the total energy differences of the neutral defect at excited and ground states, the emission energies from intra-defect state transition are obtained, reasonably explaining the photoluminescence peaks in PE. In order to study the luminescence emitted in charge recombination processes, we characterize PE defect levels in terms of thermodynamic and optical charge transition levels that involve total energy calculations of neutral and charged defects. Calculations are performed at several levels of theory including those involving (semi)local and hybrid electron exchange-correlation functionals, and many-body perturbation theory. With these critical elements, the emission energies are computed and further used to clarify and confirm the origins of the observed electroluminescence and thermoluminescence peaks. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4931986]

I. INTRODUCTION

Polyethylene (PE) is an important insulation material that has found widespread use in electrical applications including transmission line cables and capacitors.¹ The electrical performance of PE over the long term is affected by impurities and chemical defects that are originally part of the material, as well as those that are created progressively with time. Such defects can introduce charge carrier (or defect) states within the band gap of PE, can act as traps and sources of charge carriers, catalyze further damage, and can deleteriously affect the overall conduction behavior of the insulator.^{2–6} It is thus critical that a firm understanding of the nature of such defects be obtained.

The best evidence for the presence of chemical defects (especially in PE), and a knowledge of their type, is provided by a variety of luminescence measurements, including photoluminescence (PL), electroluminescence (EL), and thermoluminescence (TL).^{7–10} Defects, depending on their type and the specific details of the energetic placement of their defect levels, lead to characteristic emission signatures. Such optical measurements have led to the identification of a plethora of defects in PE, the chief among them being the carbonyl, dienone, vinyl, hydroxyl, etc., as illustrated in Fig. 1. Nevertheless, assignments of the luminescence emission bands are never straightforward, and an alternate check of whether a particular defect will lead to a particular emission peak or band is highly desired.

Such an alternate route to identify emission signatures can be provided by first principles computations, e.g., those based on density functional theory (DFT).^{11,12} Indeed, DFT and beyond-DFT computations have played a critical role in successfully unraveling the repercussions and signatures of defects in inorganic semiconductors and insulators in the past.^{13–15} In the case of PE, such work is in a state of infancy.^{16–20} Past DFT work on PE is dominated by the use of (semi)local exchange-correlation (XC) functionals to treat the quantum mechanical part of the electron-electron interaction within a single-particle framework. Defect states are identified as the one-electron Kohn-Sham eigenenergies and the emissions are then assumed to associate with the transitions involving these defect states and either the conduction band minimum (CBM) or the valence band maximum (VBM).^{17–20} While this approach does provide a qualitative picture of the defect-derived energy levels, there are several fundamental drawbacks. The first one is that the one-electron levels of DFT have no physical meaning as they relate to the energy levels of a fictitious set of non-interacting electrons.¹² The second issue relates to the band gap problem of traditional DFT.²¹ It is well-known that the band gap of insulators is significantly underestimated, which place uncertainties on the energetic location of the defect energy levels within the band gap as well as the position of the conduction and valence band edges.^{22,23} Finally, intra-defect transitions, i.e., those involving the ground and excited states of neutral defects, are not considered. These factors clearly call into question the emission energies derived from such calculations.

In the present work, the energy emitted due to intradefect state transition is computed by total energy differences



FIG. 1. Six typical defects that occur in polyethylene are considered in this work, e.g., carbonyl, dienone, hydroxyl, double bond, conjugated double bond, and vinyl. The red, white, and grey spheres are O, H, and C atoms, respectively.

of the neutral defect at excited and ground states and used to explain the origins of PL in PE. The defect levels involving charge recombination processes are characterized in terms of thermodynamic and optical charge transition levels that involve total energy differences of charged and neutral defect calculations. It is well-known that total energy differences provide a formally correct and quantitatively better description of energy level differences in molecules and solids (including defect level placements).^{14,15,24} Exchangecorrelation functionals more advanced than the (semi)local ones used in the past are considered in the present work to critically assess the role of the level of theory adopted. Furthermore, many-body perturbation theory computations are undertaken to accurately determine the band gap of PE and its conduction and valence band edge positions.

The combination of computations undertaken here including the determination and usage of charge transition levels (rather than the one-electron levels) and energy differences of the defect at higher and lowest excited states allows us to directly and quantitatively connect with available luminescence data for PE. The present work thus leads to a clear and compelling picture of defect states in PE, thus clarifying the luminescence signatures of various defects in PE.

II. MODELS AND METHODS

A. Models

Perfect crystalline PE consists of chains of singly bonded —CH₂— groups, of which all the carbon atoms display sp^3 hybridization. In this work, $1 \times 2 \times 3$ supercells of crystalline PE, containing of 24 —CH₂— groups, are constructed with and without defects as the models for our calculations. Six kinds of defects, illustrated in Fig. 1, are typically considered to exist in PE chains. A *carbonyl* defect (C=O) is created when the two H atoms of a —CH₂— group are replaced by an O atom doubly bonded to the central C atom, which now displays sp^2 hybridization. If the two H atoms of —CH₂ are replaced by a =CH₂ group, we have a *vinyl* defect. When each of two adjacent C atoms loses one H atom, a *double bond* (—CH=CH—) may be formed between them. The combination of a double bond and a carbonyl is *dienone* (—CH=CH— C=O). In the case of a *hydroxyl* defect, a H atom is replaced by a —OH group. Along the PE chains, an alternating pattern of single and double bonds leads to *conjugated double bonds* (—CH=CH—CH=CH—).

B. DFT computations

Our DFT calculations were performed with the Vienna ab-initio simulation package (VASP).²⁵⁻²⁷ The (folded) Brillouin zone of the supercell is sampled by a $2 \times 2 \times 2$ k-point Monkhorst-Pack mesh²⁸ while plane waves with kinetic energy up to 400 eV were included in the basis set. van der Waals interactions are considered within the scheme developed by Tkatchenko and Scheffler.²⁹ Relaxed geometries were obtained with Perdew-Burke-Ernzerhof (PBE) XC functional,³⁰ which were then used to compute the thermodynamic and optical transition levels with the PBE and the Heyd-Scuseria-Ernzerhof (HSE)³¹⁻³³ XC functionals, and many-body perturbation theory GW method^{34–36} [including the single-shot GW (G_0W_0) and the fully self-consistent GW (scGW) with vertex corrections]. In the case of the HSE XC functional, we used the HSE06 version with the mixing coefficient $\alpha = 0.25$ and the screening parameter $\omega = 0.2 \text{ Å}^{-1}$. The band gap E_g of perfect PE calculated with PBE, HSE06, G₀W₀, and scGW methods are 7.00 eV, 8.39 eV, 9.02 eV, and 8.95 eV, respectively, with the scGW result being closest to the experimental value (8.80 eV).³⁷ Because the accuracy of the computed emission energies involving the charge recombination process is affected by the accuracy of electronic structure calculations of perfect PE, the scGW method (hereafter referred as GW), rather than G_0W_0 , is used in the subsequent calculations.

C. Optical transitions in PE

1. Intra-defect state transitions

By absorbing an amount of energy (E_a) , a defect in PE may be transformed from the singlet ground state S₀ into either the lowest-energy excited singlet state S1 or a higher-energy excited singlet state, e.g., S_2 — see Fig. 2(a). In the latter case, processes like vibrational relaxation or internal conversion often follow, driving the defect to S_1 . The subsequent $S_1 \rightarrow S_0$ transition may either be direct, i.e., fluorescence, or indirect, going through the triplet state T₁ state by intersystem crossing, i.e., phosphorescence. The S₀, S_1 , S_2 , and T_1 states of double bond, conjugated double bond, vinyl, and hydroxyl defects are $(\pi)^2(\pi^*)^0$, $(\pi)^{+1}(\pi^*)^{-1}$, $(\pi)^{+1}(\pi^*)^0(\sigma^*)^{-1}$, and $(\pi)^{+1}(\pi^*)^{+1}$, respectively, where the superscripts (0, 1, and 2) denote the number of electrons occupied in the corresponding state while ± represents the up/down electron spin. For carbonyl, S₁ and S₂, respectively, correspond to $(n)^{+1}(\pi^*)^{-1}$ and $(n)^{+1}(\pi^*)^0(\sigma^*)^{-1}$, while T₁ is $(n)^{+1}(\pi^*)^{+1}$ due to the existence of *n*-nonbonding orbital. However, because the carbonyl group is conjugated with a double bond in the dienone defect, the excited states of dienone



FIG. 2. (a) Energy diagram of the photoluminescence involving defect energy levels. S₀, S₁, S₂, and T₁ denote the singlet ground state, the first, and second singlet excited states, and the first triplet excited state, respectively. $E_{\rm a}$ and $E_{\rm e}$, respectively, correspond to absorption and emission energies. (b) Schematic diagram of charge recombination process: ① trapped electron-hole recombination, 2 direct tunnelling, and 3 detrapping. Er is the energy differences of the defect at different excited states. (c) A configuration coordinate diagram for a defect at charge states -1 and 0 which correspond to two equilibrium configurations $R_{q'=-1}$ and $R_{q=0}$, shown as the minima of the potential energy surfaces (cyan and olive lines). The instant transition from 0 state to -1 state gains the emission energy E_e while the configuration $R_{q=0}$ remains unchanged. After a certain amount of time, the -1 state evolves to $R_{q'=-1}$, gaining E_{rl2} from the relaxation process. Similarly, the transition from the -1 state to the 0 state by absorbing E_a happens instantly before the system can relax, gaining E_{rl1} . (d) Formation energy $E_q^f(R_q)$ as a function of Fermi energy (E_F) for a defect that has two stable charge states: 0 and -1. $E_{q}^{f}(R_{q'})$ refers to the formation energy of the defect in charge state q with the equilibrium configuration of charge state $q'(R_{q'})$, where q and q' are 0 or -1. Solid lines are the formation energies of the relaxed defects in each charge state, while the formation energies for the defect with frozen atomic configuration of initial charge state are presented with dashed lines. Both thermodynamic transition level $\mu(0/-1)$ and the relevant optical transition levels $(\mu_{(0\to-1)}^{\text{opt}} \text{ and } \mu_{(-1\to0)}^{\text{opt}})$ are shown.

are $(\pi)^{+1}(n)^2(\pi^*)^{-1}$ for S₁, $(\pi)^{+1}(n)^2(\pi^*)^0(\sigma^*)^{-1}$ for S₂, and $(\pi)^{+1}(n)^2(\pi^*)^{+1}$ for T₁.³⁸ The emission energies E_e of either the S₁ \rightarrow S₀ or the T₁ \rightarrow S₀ transition were calculated as $E_e = E_{\text{excited}} - E_{\text{ground}^*}$, where E_{excited} and E_{ground^*} are the spin polarized DFT total energy of the fully relaxed defect at its excited state (S₁ or T₁) and the DFT energy of the defect at the ground state (S₀) using the atomic configuration of the excited state, respectively.³⁹ The relaxation energy of the defect at ground state may contribute to the broad PL peaks; thus, the zero-phonon line (ZPL), given by $E_{ZPL} = E_{\text{excited}} - E_{\text{ground}}$, is also calculated and used to compare with the experimental values. Here, E_{ground} corresponds to the DFT energy of the fully relaxed defect at ground state.

2. Charge recombination processes

Photon emission can also be associated with charge recombination as in EL and TL. The scenario, as sketched

in Fig. 2(b), is rather complicated with the involvement of the defect energy levels. The free charges in the conduction band, which were pumped from either the valence band by x-ray or γ -irradiation radiation in TL or the electrodes in EL, may be trapped by (shallow or deep) defect levels. While the trapped electrons can recombine directly with holes in the valence band (1) process), those from deep traps can also be transferred to the excited states of the recombination centers by direct tunneling before relaxing to the lowest-excited level for the final recombination (2) process). Electrons from shallow traps, on the other hand, can move to the excited states of the recombination centers by going through the conduction band (3 process). In reality, the electronic transitions between different energy states (i.e., defect levels, CBM, and VBM) can occur in two ways, differing by the time scale of the measurement process. Thermodynamic transitions (involving long time scales) will evolve the initial to the final charge state at its respective equilibrium geometries. Optical transitions will occur at much shorter time scales, bringing the system to the final charge state while retaining the equilibrium geometry of the initial charge state (see Fig. 2(c)). Clearly, determining the defect level positions accurately is the key to evaluate the emission energies from the charge recombination processes.

Similar to the case of intra-defect transitions, a formally correct approach to determine the defect levels and the associated transition energies is via total energy differences of PE with defects at initial and final charge states.^{13,14,40} The local equilibrium atomic configurations are different for the defects in different charge states, 13 as illustrated in Fig. 2(c). A configuration-coordinate diagram of a defect in two charge states, 0 (q) and -1 (q'), is shown in Fig. 2(c), in which the minima of the potential energy surfaces represent the ground state of the defect in charge state q = 0 and q' = -1. In the case of thermodynamic transition, the defect has enough time to relax from its initial ground state at q = 0 into its new ground states at q' = -1 or vice versa, as shown using red double arrowhead line in Fig. 2(c). In order to get this charge transition level, the formation energies $E_a^{\rm f}(R_q)$ as a function of Fermi energy (E_F) for this defect at charge states q = 0and q' = -1 are computed and shown in Fig. 2(d), where R_q represents the equilibrium structures in charge state q. Based on Fig. 2(c), the thermodynamic transition level $\mu(0/-1)$ corresponds to the crossover point between $E_{q=0}^{f}(R_{q=0})$ and $E_{a'=-1}^{f}(R_{q'=-1})$ (solid lines in Fig. 2(d)).

In general, the thermodynamic transition levels $\mu(q/q')$ is the Fermi energy at which defects in two different charge states q and q' are at thermodynamic equilibrium and are given by^{13,14,40}

$$\mu(q/q') = \frac{E_q^{t}(R_q) - E_{q'}^{t}(R_{q'})}{q - q'}.$$
(1)

Here, $E_q^f(R_q)$ is the formation energy of the *q*-charged defect at its equilibrium structure R_q , which can be obtained from DFT calculations. The Fermi energy is taken from VBM to CBM of defect-free PE. In this work, all energies are referenced to the averaged electrostatic potential of PE far away from the defect location. The electrostatic interactions of charged defects due to the periodicity and the finite supercell sizes are corrected by first-order monopole corrections in all defect cases considered. The correct positions of the defect levels with respect to the VBM and CBM are needed to explain the transitions between these energy levels. Because DFT at the PBE and HSE06 levels does not offer such information due to the incorrect position of VBM (and of course, CBM), and as the GW method does not provide total energy, we computed the transition level with PBE and HSE06 and then amended the obtained positions by the VBM shifts ($\Delta E_{VBM} = VBM_{GW} - VBM_{HSE06}$) when the GW method is used, expressed as

$$(\mu(q/q'))_{\rm GW} = (\mu(q/q'))_{\rm HSE06} + \Delta E_{\rm VBM}.$$
 (2)

The subscripts (HSE06 and GW) are refer to the method used to calculate the relevant quantities.

In the case of optical transition, the atomic configuration of the defect at the initial charge state *q* is fixed even though charge transition exists, i.e., it is a vertical transition which is shown using a blue arrowhead line in Fig. 2(c). Because the optical transition depends on the direction of charge transfer, two kinds of optical energies are possible, as shown in Fig. 2(c): emission energy (E_e) for charge transfer from initial state 0 to final state -1 and absorption energy (E_a) for the reverse process. The method to determine the optical transition level is similar to the previous case, but the energy of the final state is computed using the equilibrium structure of the initial state, such as $\mu_{(0 \rightarrow -1)}^{opt}$ and $\mu_{(-1 \rightarrow 0)}^{opt}$ in Fig. 2(d). Therefore, the optical transition level from initial state *q* to final state *q'* is defined as

$$\mu_{(q \to q')}^{\text{opt}} = \frac{E_q^{\text{t}}(R_q) - E_q^{\text{t}}(R_q)}{(q' - q)},$$
(3)

where $E_{q'}^{f}(R_q)$ is the defect formation energy in the charge state q' corresponding to the equilibrium structure R_q of the initial charge state q. The corresponding GW optical transition level is then expressed as

$$(\mu_{(q \to q')}^{\text{opt}})_{\text{GW}} = (\mu_{(q \to q')}^{\text{opt}})_{\text{HSE06}} + \Delta E_{\text{VBM}}.$$
 (4)

III. RESULTS AND DISCUSSIONS

A. Intra-defect state transition

To explain the physical origin of the observed PLphosphorescence peaks in PE, the total energy differences of various neutral defects at their ground and excited states were calculated with the PBE and HSE06 functionals. The emission energies and the ZPL of triplet to ground state transition $(T_1 \rightarrow S_0)$ for all defects are shown in Table I, together with experimental PL results. The dienone case alone presented convergence issues with HSE06 functional, and hence, this result is not presented in Table I. However, given the reasonable correlation between the PBE and HSE06 results, the PBE results for this defect may be viewed as acceptable. For ease of visualization, the PBE results of the defect at excited and ground state are also shown in Fig. 3. The experimental PL levels in Fig. 3 are determined by the energy differences between the experimental emission energy and the S₀ ground state.

TABLE I. Computed emission energies (E_e) and zero-phonon line (E_{ZPL}) from intra-defect state transition $(T_1 \rightarrow S_0)$, given in eV, together with available experimental photoluminescence (PL) results. Computed results for dienone with HSE06 are not available since convergence issues were encountered for this case.

		$E_{ m e}$		EZPL		
Defects	PBE	HSE06	PBE	HSE06	Experiments	
Carbonyl	2.27	2.15	3.27	3.29	2.06-3.10 ^a	
Dienone	2.51		2.82		2.25-3.54 ^a	
Hydroxyl	0.57	0.03	4.69	4.57		
Conjugated double	1.71	1.51	2.17	2.09	2.90 ^b	
bond						
Double bond	0.14	0.03	2.71	2.61		
Vinyl	0.02	0.03	0.05	0.03		

^aReference 42.

^bReference 43.

The consistency between the computed and experimental emission energies of carbonyl and dienone defects indicates that the PL emission bands of dienone and carbonyl involve the transition from the $(\pi)^{+1}(\pi^*)^{+1}$ excited state to the $(\pi)^2(\pi^*)^0$ ground state, and the transition from the $(n)^{+1}(\pi^*)^{-1}$ excited state to the $(n)^2(\pi^*)^0$ ground state, respectively. A small discrepancy between the computed and the measured results for conjugated double bond defect still remains. Possible reasons for this disagreement might include some uncertainties in the experimental data, or more likely, because in the present calculations, the defects are modeled in the crystalline PE environment. Nevertheless, we can conclude that the luminescence data for conjugated double bond defect are related to the transition from the $(\pi)^{+1}(\pi^*)^{+1}$ excited state to the $(\pi)^2(\pi^*)^0$ ground state. For hydroxyl, double bond, and vinyl defects, the low vertical transition energies, i.e., $E_{\rm e}$, indicate that the relaxation from triplet to ground states may either be radiationless or hard to detect.

B. Charge recombination processes

1. Defect geometries

The relaxed structures of PE with defects at different charge states q [denoted by $(defect)^q$, q = 0, -1, and +1] are shown in Fig. 4. The variation of geometry parameters (bond angle \angle and bond length l) of (defect)^q indeed shows that the equilibrium structures corresponding to different charge states are different. For example, the C=O bond length of carbonyl increases from 1.228 Å for the neutral state to 1.315 Å for the -1 charge state, because the extra electron is localized at the C=O bond and leads to bond weakening. Whereas, compared to the $(carbonyl)^0$, the decrease of the C=O bond length in $(carbonyl)^{+1}$ is due to the loss of an electron. As another example, we note that a rotation of about 90° can be observed for C=C part of (double bond)⁻¹ and $(\text{double bond})^{+1}$ compared to the neutral case. This is because both positive and negative charges can weaken the C=C bond and make the PE chain free to rotate. All these relaxations for $(defect)^q$ make contribution to the broad luminescence peaks in experiments. Therefore, in this work, all levels ranging from



FIG. 3. Neutral defect ground and excited states (S₀, S₁, S₂, and T₁ states) involved in the intra-defect transitions are shown with black solid lines. The S₀ states are aligned with the $\mu(0/+1)$ levels of defects. The thermodynamic (i.e., $\mu(0/-1)$ and $\mu(0/+1)$) and optical (i.e., $\mu_{(0)--1)}^{opt}$, $\mu_{(0)-+1)}^{opt}$, and $\mu_{(+1-0)}^{opt}$) charge transition levels are represented with blue, wine, red, magenta, violet, and orange solid lines, respectively. The VBM and CBM are given with respect to the average electrostatic potential. The possible transition levels which lead to optical emissions are represented by the shaded region. The energy differences between the PL level and S₀ state correspond to experimental emission energy. The experimental EL levels for carbonyl and dienone defects are determined by the differences between the $\mu(0/+1)$ and experimental emission energies,⁴¹ while the experiment TL level of vinyl is obtained by the differences between the GW CBM (or VBM) and experimental emission energy.⁴² For completeness, the Kohn-Sham unoccupied and occupied states are also shown using black and red dashed lines, respectively.

 $\mu_{(q \to q')}^{\text{opt}}$, which is relevant to the emission energy, to $\mu(q/q')$ are used to compare with experimental results.

2. Charge transition levels

In order to characterize the defect levels in PE, which are responsible for the observed luminescence signatures (especially the EL and TL through charging/discharging of the defect levels as per the mechanisms outlined in Fig. 2(b)), the thermodynamic and optical transition levels for the six typical defects in PE have been calculated. The results obtained from various methods (solid lines) and available EL and TL experimental data are shown in Fig. 3. As can be seen, the (0/+1) charge transition levels for carbonyl, dienone, conjugated double bond, and double bond are close to the VBM, indicating that these four defects are easy to lose an electron and become positive charge state. The associated thermodynamic (i.e., $\mu(0/-1)$ and $\mu(0/+1)$) and optical (i.e., $\mu_{(0\to-1)}^{\text{opt}}$, $\mu_{(0\to+1)}^{\text{opt}}$, $\mu_{(0\to+1)}^{\text{opt}}$, and $\mu_{(+1\to0)}^{\text{opt}}$) transition levels are represented with blue, wine, red, magenta, violet, and orange solid lines, respectively. Because of the broad peak observed in experiments, the levels from $\mu_{(-1\rightarrow 0)}^{\text{opt}}$ to $\mu(0/-1)$ or from $\mu_{(+1\rightarrow 0)}^{\text{opt}}$ to $\mu(0/+1)$ are used to compare with experimental levels, as shown by the shaded region in Fig. 3.

Given the computed defect level placements, excited state energies, and the measured luminescence signatures portrayed in Fig. 3 in a unified manner, we propose that the mechanism ⁽²⁾ in Fig. 2(b) underlies the EL spectra

of PE containing carbonyl, dienone, hydroxyl, conjugated double bond, and double bond defects, and that mechanism ① underlies the measured TL spectra of PE containing vinyl defects. More specifically, in the former cases (when we believe mechanism 2 is in operation), an electron from the $\mu_{(-1 \rightarrow 0)}^{\text{opt}}$ of such defects may first tunnel to their (energetically well-positioned) S_2 excited state, then pass to the triplet (T_1) excited state by internal conversion and intersystem crossing, and finally transfer to the $\mu_{(+1\rightarrow 0)}^{\text{opt}}$ level, accompanied by with emission of photons, i.e., $(defect)^{-1} + (defect)^{+1} \rightarrow (defect)^{0}$. The entire process can be represented by $(0/-1) \rightarrow S_2$ \rightarrow S₁ \rightarrow T₁ \rightarrow (0/ + 1), with the last step leading to the observed EL signature. On the other hand, in the case of the vinyl defect, both $\mu_{(0\to-1)}^{\text{opt}}$ and $\mu_{(+1\to0)}^{\text{opt}}$ are close to the experimental result. This implies that the transitions of electrons from the conduction band to the $\mu^{\text{opt}}_{(+1\rightarrow 0)}$ of vinyl and electron transferred from $\mu^{\text{opt}}_{(-1 \rightarrow 0)}$ to the valence band are both likely the origin of the luminescence caused by the vinyl defect. In other words, we use the computed defect charge transition level and excited state placements to arrive at the simplest theory that matches with observations. The proposed recombination pathways, the computed transition/emission energies (at various levels of theory), and available measured EL and TL signatures are listed in Table II.

It is also worth noting a few curious details related to the computed results. When referenced to the average electrostatic potential, the charge transition levels calculated with PBE agree well with those based on the HSE06, and the GW



FIG. 4. Side view of the relaxed PE model with defects at different charge states [denoted by $(defect)^q$, q = 0, -1, and +1], optimized with PBE functional. The red, white, and grey spheres are, respectively, O, H, and C atoms. The bond angles (\angle) and bond lengths (l, given in Å) are shown in red and black, respectively.

method, as shown in Fig. 3. Unlike the charge transition levels, a remarkable variation (with the level of theory used) of the band edges of PE is observed in Fig. 3, which may impact the comparison with experimental emission energies. To show the role of band edges, the emission energies of defects computed with the PBE, HSE06, and the GW method are listed in Table II, together with available experimental results. For carbonyl, dienone, hydroxyl, conjugated double bond, and double bond defects, the emission energy ranges from $\mu_{(-1\to0)}^{\text{opt}} - \mu_{(+1\to0)}^{\text{opt}} - E_{\text{r}} \text{ to } \mu(0/-1) - \mu(0/+1) - E_{\text{r}}, \text{ where } E_{\text{r}}$ is the energy differences of the fully relaxed defect at S₂ and T_1 excited states, calculated with spin polarized PBE and HSE06 functionals.³⁹ In the case of vinyl, the emission energy ranges from CBM – $\mu_{(+1\rightarrow 0)}^{\text{opt}}$ to CBM – $\mu(0/+1)$, or from $\mu_{(-1\rightarrow 0)}^{\text{opt}}$ – VBM to $\mu(0/-1)$ – VBM. We note that the computed emission energies of carbonyl, dienone, and vinyl with all functionals agree well with experimental values. This indicates that both charge transition levels and emission energies are captured well by the PBE functional, if a suitable reference energy is used.

3. Kohn-Sham levels

To complete the discussion, and to put our work in the context of the existing literature pertaining to defects and defect states in PE, we also include the one-electron Kohn-Sham defect levels for various defects in PE in Fig. 3. These are shown using black (unoccupied states) and red (occupied states) dashed lines in Fig. 3. While the Kohn-Sham defect levels are in reasonable and qualitative agreement with the charge transition levels, some important observations should be made. First, even when the PBE and HSE06 average electrostatic potentials are aligned, the one-electron levels do not line up (unlike the charge transition levels). This indicates that the one-electron levels are strongly dependent on the level of theory used. Second, the emission energies that one would arrive at purely using the one-electron energies and the band edges of the same theoretical treatment would be in stark disagreement with experiments. Thus, interpreting defect spectroscopic signatures using Kohn-Sham levels should be performed with cautions.

TABLE II. Computed emission energies (E_e) from charge recombination processes, given in eV, with available experimental results. The existence of E_e range is because from $\mu_{(-1\to0)}^{opt}$ to $\mu(0/-1)$ or from $\mu_{(+1\to0)}^{opt}$ to $\mu(0/+1)$ is used to compare with experiments. EL and TL stand for electroluminescence and thermoluminescence, respectively.

Defects					
	Path	PBE	HSE06	GW	Experimental values
Carbonyl	$(0/-1) \rightarrow S_2 \rightarrow S_1 \rightarrow T_1 \xrightarrow{E_e} (0/+1)$	2.29-3.08	2.18-3.12	2.18-3.12	2.92 ^a (EL)
Dienone	$(0/-1) \rightarrow S_2 \rightarrow S_1 \rightarrow T_1 \xrightarrow{E_e} (0/+1)$	2.30-2.63	2.22-2.79	2.22-2.79	2.43 ^a (EL)
Hydroxyl	$(0/-1) \rightarrow S_2 \rightarrow S_1 \rightarrow T_1 \xrightarrow{E_e} (0/+1)$	4.63	3.48	3.48	
Conjugated double bond	$(0/-1) \rightarrow S_2 \rightarrow S_1 \rightarrow T_1 \xrightarrow{E_e} (0/+1)$	2.34-2.90	1.76-2.51	1.76-2.51	
Double bond	$(0/-1) \rightarrow S_2 \rightarrow S_1 \rightarrow T_1 \xrightarrow{E_e} (0/+1)$	2.48-3.03	2.08-2.73	2.08-2.73	
Vinyl	$CBM \xrightarrow{E_e} (0/+1)$	4.58-4.72	5.23-5.37	6.28-6.42	4.13–6.02 ^b (TL)
	$(0/-1) \xrightarrow{E_{e}} VBM$	5.43-5.54	6.53-6.65	6.04-6.16	
^a Reference 41.					

^bReference 42.

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IF 137.99.44.177 On: Wed. 30 Sep 2015 13:15:17

IV. SUMMARY

In summary, we have presented a detailed first-principles computational study of chemical defects in PE and have quantitatively determined the emission and absorption energies derived from intra-defect state transition and charge recombination processes. For the intra-defect state transition, the emission energies are calculated by total energy differences of the neutral defect at excited and ground states. These results are in good agreement with the measured photoluminescence bands of PE. To assign the electroluminescence and thermoluminescence peaks involving the charge recombination process, we go beyond traditional density functional theory calculations within the one-electron framework. In particular, we determine the defect levels in terms of thermodynamic and optical charge transition levels via total energy calculations of neutral and charged defects. Consequently, by combining the defect level positions and the energy differences of defects at higher and lowest excited states, the most likely emission mechanisms and emission energies have been determined, leading to excellent correspondence with available experimental results. Finally, we suggest that this computational scheme may be used to interpret the luminescence data of other organic polymers as well.

ACKNOWLEDGMENTS

This work is supported by a Multidisciplinary University Research Initiative (MURI) grant from the Office of Naval Research. Discussions with Christian Laurent and Gilbert Teyssedre are gratefully acknowledged. The authors also thank one of the anonymous reviewers, whose diligent comments have lead to significant improvements in the quality, reach, and impact of the manuscript.

- ¹A. Peacock, *Handbook of Polyethylene: Structures: Properties, and Applications* (CRC Press, New York, 2000).
- ²R. Patsch, J. Phys. D: Appl. Phys. 23, 1497 (1990).
- ³M. Ieda and Y. Suzuoki, IEEE Electr. Insul. Mag. 13, 10 (1997).
- ⁴L. Dissado, G. Mazzanti, and G. Montanari, IEEE Trans. Dielectr. Electr. Insul. **4**, 496 (1997).
- ⁵D. Ceresoli, E. Tosatti, S. Scandolo, G. Santoro, and S. Serra, J. Chem. Phys. **121**, 6478 (2004).
- ⁶G. Mazzanti and G. Montanari, IEEE Trans. Dielectr. Electr. Insul. **12**, 876 (2005).
- ⁷M. Taleb, G. Teyssedre, S. Roy, and C. Laurent, IEEE Trans. Dielectr. Electr. Insul. **20**, 311 (2013).

- ⁸N. Allen, J. Homer, J. McKellar, and D. Wood, J. Appl. Polym. Sci. **21**, 3147 (1977).
- ⁹G. Teyssedre, G. Tardieu, and C. Laurent, J. Mater. Sci. 37, 1599 (2002).
- ¹⁰B. Qiao, G. Teyssedre, and C. Laurent, J. Phys. D: Appl. Phys. 48, 405102 (2015).
- ¹¹P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
- ¹²W. Kohn and L. Sham, Phys. Rev. **140**, A1133 (1965).
- ¹³C. Freysoldt, B. Grabowski, T. Hickel, J. Neugebauer, G. Kresse, A. Janotti, and C. G. Van de Walle, Rev. Mod. Phys. 86, 253 (2014).
- ¹⁴R. Ramprasad, H. Zhu, P. Rinke, and M. Scheffler, Phys. Rev. Lett. 108, 066404 (2012).
- ¹⁵Q. Yan, A. Janotti, M. Scheffler, and C. G. Van de Walle, Appl. Phys. Lett. 105, 111104 (2014).
- ¹⁶C. R. Bealing and R. Ramprasad, J. Chem. Phys. 139, 174904 (2013).
- ¹⁷A. Huzayyin, S. Boggs, and R. Ramprasad, IEEE Trans. Dielectr. Electr. Insul. **17**, 926 (2010).
- ¹⁸A. Huzayyin, S. Boggs, and R. Ramprasad, IEEE Trans. Dielectr. Electr. Insul. **17**, 920 (2010).
- ¹⁹M. Meunier, N. Quirke, and A. Aslanides, J. Chem. Phys. 115, 2876 (2001).
- ²⁰J. Anta, G. Marcelli, M. Meunier, and N. Quirke, J. Appl. Phys. **92**, 1002 (2002).
- ²¹A. Seidl, A. Görling, P. Vogl, J. Majewski, and M. Levy, Phys. Rev. B 53, 3764 (1996).
- ²²M. S. Hybertsen and S. G. Louie, Phys. Rev. Lett. 55, 1418 (1985).
- ²³M. Grüning, A. Marini, and A. Rubio, J. Chem. Phys. **124**, 154108 (2006).
 ²⁴Q. Yan, A. Janotti, M. Scheffler, and C. G. Van de Walle, Appl. Phys. Lett.
- **100**, 142110 (2012).
- ²⁵G. Kresse, "Ab initio molekular dynamik für flüssige metalle," Ph.D. thesis, Technische Universität Wien, 1993.
- ²⁶G. Kresse and J. Furthmüller, J. Comput. Mater. Sci. 6, 15 (1996).
- ²⁷G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
- ²⁸H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
- ²⁹A. Tkatchenko and M. Scheffler, Phys. Rev. Lett. **102**, 073005 (2009).
- ³⁰J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
- ³¹J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **118**, 8207 (2003).
 ³²J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. **124**, 219906 (2006).
- ³³A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, J. Chem. Phys. **125**, 224106 (2006).
- ³⁴L. Hedin, Phys. Rev. **139**, A796 (1965).
- ³⁵M. S. Hybertsen and S. G. Louie, Phys. Rev. B 34, 5390 (1986).
- ³⁶M. van Schilfgaarde, T. Kotani, and S. Faleev, Phys. Rev. Lett. **96**, 226402 (2006).
- ³⁷K. Less and E. Wilson, J. Phys. C 6, 3110 (1973).
- ³⁸F. A. Carey and R. J. Sundberg, *Advanced Organic Chemistry: Part A:*
- Structure and Mechanisms (Springer Science & Business Media, 2007).
 ³⁹A. Gali, E. Janzén, P. Deák, G. Kresse, and E. Kaxiras, Phys. Rev. Lett. 103, 186404 (2009).
- ⁴⁰C. G. Van de Walle and J. Neugebauer, J. Appl. Phys. **95**, 3851 (2004).
- ⁴¹C. Laurent, G. Teyssedre, S. Le Roy, and F. Baudoin, IEEE Trans. Dielectr. Electr. Insul. **20**, 357 (2013).
- ⁴²C. Laurent, C. Mayoux, and S. Noel, J. Appl. Phys. 58, 4346 (1985).
- ⁴³T. Ito, D. Kaneko, and Y. Ohki, in 2002 Annual Report Conference on Electrical Insulation and Dielectric Phenomena (IEEE, Quintana Roo, Mexico, 2002), pp. 856–860.