

Trapping of excitons at chemical defects in polyethylene

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In a previous paper we studied an injected electron-hole pair in crystalline polyethylene (PE) and found that the exciton becomes weakly self-trapped in a narrow interchain pocket comprised between two *gauche* defects. Despite the large energy stored in the trapped excitation, there did not appear to be a direct nonradiative channel for electron-hole recombination. Actual polyethylene systems of practical use are, however, neither crystalline nor pure. To understand the fate of an electron-hole pair in the impure case, we studied by *ab initio* simulations the evolution of an exciton trapped on three common chemical defects found in polyethylene: a grafted carbonyl (C=O); an intrachain vinyl group (C=C); a grafted carboxyl (COOH). *Ab initio* simulations lead to predict three different outcomes: trapping, nonradiative recombination, and homolytic bond-breaking, respectively. This suggests that extrinsic self-trapping of electron-hole pairs over chemical defects inside the quasicrystalline fraction of PE could be relevant for electrical damage in high-voltage cables. © 2004 American Institute of Physics. [DOI: 10.1063/1.1783876]

I. INTRODUCTION

On account of its large band gap (≈ 9 eV), its chemical inertness, and its easy processing, polyethylene (PE) is the material of choice in extruded electric cables for high-voltage applications. The highly insulating properties of PE, however, do not prevent a tiny flow of charge carriers, both electrons and holes, injected at the very high electric fields realized under normal high voltage operation conditions. Understanding and controlling this flow and its consequences is, of course, extremely important for improving the cable performances. It is known, for example, that lifetime against dielectric breakdown depends crucially on the mobility of the injected charge carriers. Aging and eventual failure of the cable is believed to be connected to local damage induced by charge flow and/or recombination.¹

In a previous paper, we addressed the basic electronic properties of PE which underlie the observed phenomenology. In particular, we studied there the detailed nature of the electronic states corresponding to the highest valence-band state (holes), to the lowest conduction-band states (elec-

trons), and to the simultaneous presence of holes and electrons—whose bound state we will refer to with the standard name of *excitons*.²

We found in Ref. 2 that an exciton in pure, crystalline PE becomes self-trapped by spontaneously inducing a local distortion of one of the polymeric chains three $-\text{CH}_2-\text{CH}_2-$ units apart. At least within the short time lapse (less than 10 ps) allowed by *ab initio* molecular dynamics simulation, this intrinsic defect did not appear to provide a viable channel for nonradiative electron-hole recombination (NREHR). Should the electron-hole recombination energy, amounting to several electronvolts, be eventually released in a nonradiative channel, and thus suddenly turned into ionic kinetic energy, it would surely fuel important local structural and eventual electric damage. The possible existence of channels for this kind of damage must therefore be actively explored.

In this paper, we study the behavior and the evolution of an exciton in *imperfect* and *impure* PE. The reason for this is twofold. On one hand, imperfections and impurities are ubiquitous in this material, both as a result of physical processing and of deliberate chemical doping. On the other hand, defects may provide sites with deep lying mid-gap electronic states that will make for very effective electron and hole

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traps. Once occupied, these traps may effectively be short-lived, leading to fast local distortions, thus possibly acting as stepping stones to nonradiative recombination.

The main characteristic of real PE is its general lack of crystallinity. Crystalline lamellae are embedded in a prevalently amorphous material,¹ where the PE chains are generally misfolded. The lowest density regions at the crystalline-amorphous interfaces have been argued to give rise to localized electronic states. These states will attract and bind electrons in virtue of the negative electron affinity of bulk crystalline PE.³ While these extended interfaces therefore act as shallow electron traps, they do not appear to give rise to NREHR.² In this work we shall therefore concentrate on *local* defects, chosen so as to represent a certain variety of behavior that may be more generally expected.

We considered three specific cases: First, a *carbonyl* defect group C=O, that is commonly introduced in PE through branching agents. Next, the very common *vinyl* defect, arising when two neighboring carbons become double-bonded instead of single-bonded, with loss of the two corresponding hydrogens (eliminated as H₂). Finally, we studied the carboxyl group (—COOH), prototype of more electronegative groups than carbonyl, which should therefore trap electrons in a deeper state.

All the defects considered were found to exhibit localized states deep inside the PE band gap, and will also attract and bind an initially free, delocalized electron-hole pair. Following that binding, however, each of the trapped-exciton primed defects leads to a different epilogue. Trapping is simply stable in the carbonyl defect, without NREHR. There is instead nondissociative NREHR in the vinyl group. Finally, there is NREHR with subsequent violent dissociation and detachment of the group in the case of carboxyl.

We present material in the following order: First, we shall describe in Sec. II the methods and computational techniques used. In Sec. III we will study the exciton in chemically modified PE, and show its trapping and its evolution eventually leading to a nonradiative recombination. Section IV will be devoted to a short discussion of the possible consequences, and to our conclusions.

II. COMPUTATIONAL TECHNIQUES

Our tool will be atomistic simulation, in particular *ab initio* molecular dynamics (MD) simulation of the Car-Parrinello variety.⁴ To be sure, this technique is strictly speaking suitable only to describe evolution of a system where the electrons are in their instantaneous ground state. We shall instead use it here in a heuristic extension, where the presence of an electron-hole pair excitation is forced through incomplete electron occupancy, with radiative recombination explicitly forbidden, as will be explained further below. Other standard limitations of *ab initio* MD are very small system sizes (limited to a few hundred electrons per cell, with periodic boundary conditions) and very short time durations (of order 1 ps) of the simulation dynamics. Despite these limitations, the simulation results obtained with the present method are very revealing and generally instructive on the presence or absence of NREHR. The exciton-induced atomic motions and distortions generally

take place much faster than 1 ps, and also enough localized within the simulation cell, that the size and time limitations do not appear too serious (longer simulations would not make sense anyway while ignoring radiative recombination). The atomic rearrangements are also generally unexpected, involving novel concerted atom motions enacted by the system in the effort to lower the potential energy provided by the initial exciton state. We carried out first-principle electronic structure calculations of PE, using state-of-the-art density-functional methods,⁵ based on plane-wave expansion and pseudopotentials. Technical details are similar to those given in previous papers.^{6–8} Calculations were carried out within the “BLYP” gradient corrected energy functional.⁹ The ion-electron interactions were described by norm-conserving Martins-Troullier pseudopotentials.¹⁰ Wave functions were expanded in plane waves, with a plane-wave energy cutoff of 70 Ry. Structural optimization and MD were carried out with a steepest descent and a Car-Parrinello algorithm,¹ respectively. The time step for the Car-Parrinello dynamics was set to 5 a.u. (0.6 fs) and the electronic mass to 200 atomic units. *Ab initio*, finite-temperature MD simulations were carried out with the help of a Nosé thermostat with a fictitious mass corresponding to a frequency of 40 THz, unless otherwise specified.

The van der Waals physical attraction between the chains—a numerically small but qualitatively important contribution to the stability of PE which is not accounted for by quasilocal approximations to the DFT functional such as BLYP—was included empirically through an extra two-body interatomic potential with a parametrized r^{-6} tail of the form,

$$V_{vdw} = -\frac{1}{2} \sum_{i,j} \frac{C_{i,j}}{r_{i,j}^6} f_c(r_{i,j}), \quad (1)$$

where f_c is a function cutting off at short distance. All the parameters entering (1) were given the same values as in Serra *et al.*,⁶ optimized to correctly reproduce the equilibrium structure, stability, elastic constants, and thermal properties of neutral PE. This ensures that our calculations are based on a sound overall physical description of PE, prior to the excitation consisting of the simultaneous introduction of an electron and a hole.

Basic questions we faced in the present excited-state calculations are (i) how to introduce the electron-hole pair, and (ii) how to decide whether or not there will be NREHR within our simulation approach:

(i) *How to introduce the electron-hole pair.* A natural choice for the introduction of an electron-hole pair would be to introduce and to evolve a triplet exciton. Theoretically, the triplet exciton is the $S=1$ ground state in a nonmagnetic insulator, and can thus in full legitimacy be introduced in a ground-state calculation by forcing a total spin of one.¹¹ Experimentally, triplet excitons could, for example, be generated by energy loss exchange processes by impact of low-energy electrons,¹² whereby an incoming spin down electron drops in energy to occupy an empty conduction state, while kicking upward in energy a spin up valence electron, which creates the hole. Although with an energy and lifetime that are presently unknown, a long-lived triplet $S=1$ exciton

must exist in PE, as it does in all other molecular solids, with an excitation energy somewhat below the ordinary, singlet exciton, and thus below the band gap of 8.8 eV. Computational limitations forced us, however, to postpone such a costly spin-polarized procedure, and to consider a simpler alternative shortcut solution. We mimicked the presence of a singlet exciton by replacing the ground-state occupancy of two electrons per state up until the valence band top with an occupancy of one electron, instead of two, for the valence band top and for the conduction band bottom, that is for what were originally the highest occupied and the lowest Kohn-Sham (KS) eigenvalues in a non-spin-polarized ground-state calculation.

This approximation presents, in principle, two problems. The first is that the Hellmann-Feynman forces calculated in this manner differ in principle from the true ones in an excited state that could nowadays be accessed in the *GW* approximation¹³ or in time-dependent density functional theory (TDDFT).^{14,15} Up to now such calculations are limited to small molecules of few atoms; nevertheless the geometries of the organic groups in the excited state obtained by our method compare very well with those obtained by *GW* and TDDFT at the price of a larger computational cost. The second is a spin-contamination problem related to the fact that such an exciton is, in a nonpolarized calculation, neither a singlet nor a triplet state.¹⁶ In pure crystalline PE it could be argued² that spin-contamination effects were negligible owing to a reduced electron-hole exchange interaction.¹⁷ That is due in turn to the different nature of the electron (of interchain character) and of the hole (of intrachain character)⁷ causing a very reduced overlap. Electron-hole overlap will, however, increase substantially in the present case, when both electron and hole become localized onto a chemical defect. That will also increase the singlet-triplet energy separation, and with that the error in our calculation. Nonetheless, it is physically clear that this is not really a serious problem overall. In fact, spin contamination implies an error which is anyway smaller than the singlet-triplet exciton splitting. In PE with a large 8.8 eV band gap, that splitting, of order 1 eV, is anyway small by comparison. It is also comparable to other errors in the calculation, such as the density functional reduced gap error (which incidentally it tends to partly compensate). We thus carried out first of all the electronic structure calculations, the initial structural relaxation, and the subsequent molecular dynamics simulations of structural and electronic evolution in this model exciton state. Previous *ab initio* simulations on photo-voltaic systems¹⁸ and electron-transfer in biomolecules¹⁹ have been reported employing similar or different, but equally drastic approximations.

(ii) *How to decide whether or not there will be NREHR within our simulation approach.* The starting ground-state configuration of the PE system, with or without defects, is electronically insulating, with a large energy separation between the highest occupied and the lowest unoccupied states. In pure PE it corresponds to the band gap, whose value in the present DFT approximation is about 6.46 eV. With the defects, the gap is smaller, but still amounting to several electronvolts. Once the exciton is introduced and these two lev-

els are singly occupied, there will be electronic relaxations, as well as Hellmann-Feynman forces acting on all the nuclei in the system, whose net outcome will result in a reduction of the energy gap between these two states. The hole state will rise in particular, and the electron state will drop in order to reduce the total energy in presence of the exciton. A case where NREHR does not occur will be one where after a short simulation time (we found 0.3 ps to be generally sufficient, given the extreme rapidity of relaxations in presence of the large energy electron-hole pair) the electron and the hole levels finally remain well separated, settling to an unequivocally positive and large gap between one and the other. If on the contrary during the simulation the two levels strongly approach one another, and either cross or become nearly degenerate (actual crossing is generally impeded by their having same symmetry) then this will be taken to signify NREHR. At the crossing of the electron with the hole level the two should annihilate, and the system will relax to a new ground state without exciton, embodying in fact a classical nonradiative recombination diagram.¹⁷ A further path for NREHR would be the crossing of the ground-state potential energy surface with (an optically dark) two-electron excitation, which is quite common for double bond systems. Although feasible with our current technique, we did not investigate this mechanism as the approximations aforementioned (i.e., the neglect of spin) would become more serious for two-electron excited states.

III. RESULTS

As announced, we will proceed in this section to describe the electron-hole pair behavior in extrinsic PE, in presence of various chemical defects, namely, carbonyl, vinyl, and carboxyl defects. The behavior is different in each of these three cases, providing a good illustration of the variety of possibilities that can arise in real life.

A. Carbonyl defect

The carbonyl group C=O is commonly introduced in PE through branching agents. Branched PE is the so-called LDPE (low density PE) and has poor mechanical properties, because cross-links favor the amorphous phase with respect to the crystalline fraction. We modeled the system with two parallel PE chains made up of seven —C₂H₄— units in a periodically repeated simulation box. We substituted a CH₂ group with a carbonyl group (C=O) pointing toward the second chain [Fig. 1(a)]. We relaxed the atomic positions using a steepest-descent algorithm, first for the ground state, and then for the excited state, with the electron-hole pair. The system relaxed, but no attempt at level crossing—no NREHR—took place. In the final state, the hole wave function was tightly localized on a lone pair of the oxygen atom [Fig. 1(b)], lying 1.12 eV above the top of the valence band. The electron wave function localized instead onto a π* state [Fig. 1(c)] of the C=O bond, lying 0.53 eV below the bottom of the conduction band. This exciton is clearly trapped at the impurity and leads to a weakening of the C=O bond; in fact, the C=O bond length increases from 1.23 Å in the ground state to 1.27 Å in the excited state, a value in the range of a single C—O bond. At the same time the C=O

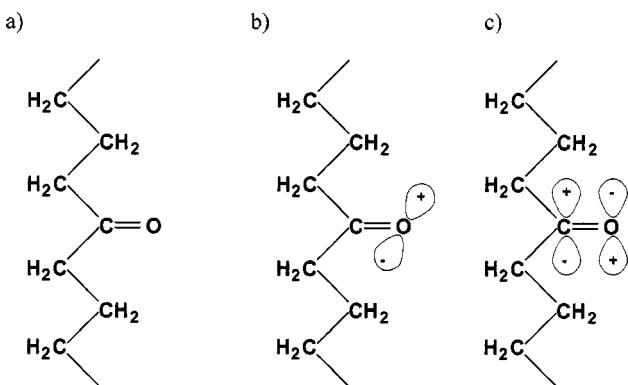


FIG. 1. (a) The carbonyl defect. (b) Schematic drawing of the HOMO (hole state). (c) Schematic drawing of the LUMO (electron state).

group deviates slightly from planarity. The energy gain with electron-hole trapping, measured as the total energy decrease from the undistorted to the distorted configuration is 0.53 eV. Starting from this trapped exciton state obtained by relaxation, we also carried out a molecular dynamics finite-temperature simulation of the carbonyl group grafted on top of a polyethylene *lamella* surface³ in presence of the trapped electron-hole pair, so as to give the system a chance to fluctuate, and eventually to break bonds if convenient. We first prepared a trial thermalized system by a 10 ps classical molecular dynamics run at 300 K with the MM3 empirical force field.²⁰ After that we carried out *ab initio* molecular dynamics for 0.3 ps without the *e-h* pair, temperature at 300 K controlled by a Nosé thermostat. Finally, we injected the *e-h* pair setting to one the occupation numbers of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) Kohn-Sham (KS) states, as explained earlier. The wave functions were quenched on the energy surface of the excited state. Finally, we performed 0.3 ps of *ab initio* molecular dynamics in the excited state in the microcanonical ensemble. The C=O bond length (Fig. 2) oscillated around 1.28 Å, a value larger than in the ground state. The KS eigenvalues also oscillated, and the minimum value of the HOMO-LUMO gap, stabilized to 3.7 eV, with no sign of closing. We conclude that the *e-h* pair should get trapped at a grafted carbonyl in PE, but it will not lead to NREHR and to damage.

B. Intra-chain vinyl defect

Another defect commonly present in PE is the so-called vinyl defect, namely, an insaturation ($-\text{CH}=\text{CH}-$), caused by removal of two successive hydrogens along the polymeric chain. We modeled the defect with two parallel PE chains made up of seven $-\text{CH}_2-\text{CH}_2-$ units in a periodically repeated simulation box. Then we removed two hydrogens from two neighboring CH_2 units. The double bond was in a trans configuration [Fig. 3(a)]; the C=C distance reduced to 1.33 Å, a value shorter than 1.53 Å of a single C=C bond. There are two shallow electronic levels associated with the vinyl defect in its ground state. The HOMO is the C=C π -bonding molecular orbital situated 0.32 eV above the top of the valence band. The LUMO is the C=C π^* -antibonding combination, situated nearly symmetrically 0.38 eV below

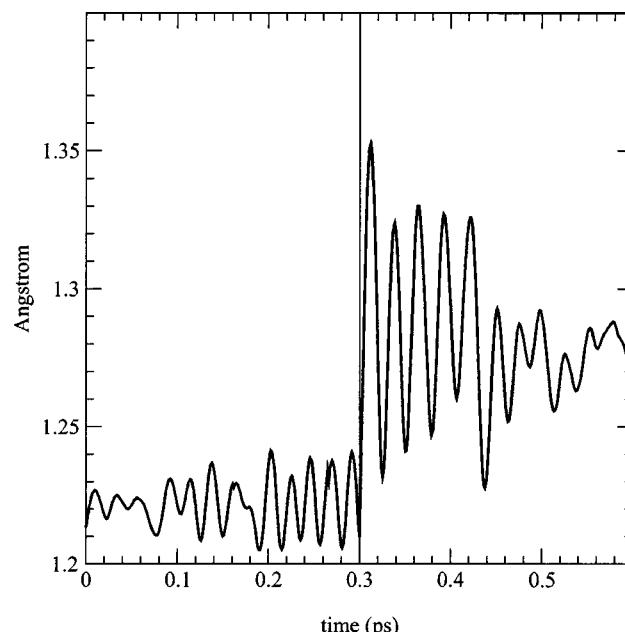


FIG. 2. C=O bond length during the MD run. The exciton was created after 0.3 ps.

the bottom of the conduction band. The torsion angle H—C=C—H is 180° corresponding to a perfect trans configuration [Fig. 3(b)]. After adding the *e-h* pair, we performed a set of structural relaxations in the excited state and we found that as expected the exciton became trapped at the vinyl defect, with a weakening of the C=C bond. The C=C distance grew to 1.51 Å, a value now close to that of a single C=C bond. The torsion angle still remained 180°, and the system gained 1.8 eV in the relaxation. However, because of the exciton undoing the double bond, the polymeric chain should now be free to rotate around the previously rigid C=C bond. Such a process had no chance to occur in relaxation, but could well take place during finite-temperature evolution of the exciton trapped on the vinyl defect. We studied that possibility by a very similar molecular dynamics simulation protocol to that used for the carbonyl. The excited state dynamics did indeed produce a characteristic evolution of the exciton-primed vinyl defect.

As can be seen in the final configuration shown in Fig. 4, the weakening of the C=C bond is now also accompanied by a 90° rotation around the C=C axis, which apparently

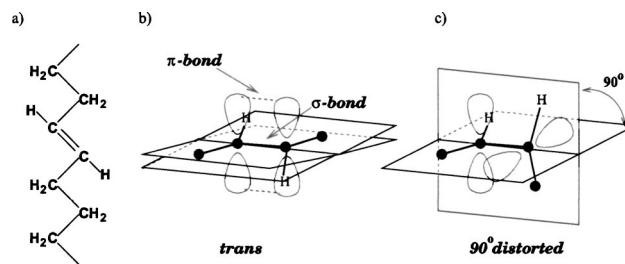


FIG. 3. (a) Chemical structure of the vinyl defect. (b) Ground state: the HOMO is the π -bonding combination on the C=C bond; the LUMO is the π^* -antibonding combination. (c) Excited state: the π is broken, leaving two dangling bonds. The two segments of the PE chain are rotated by about 90°.

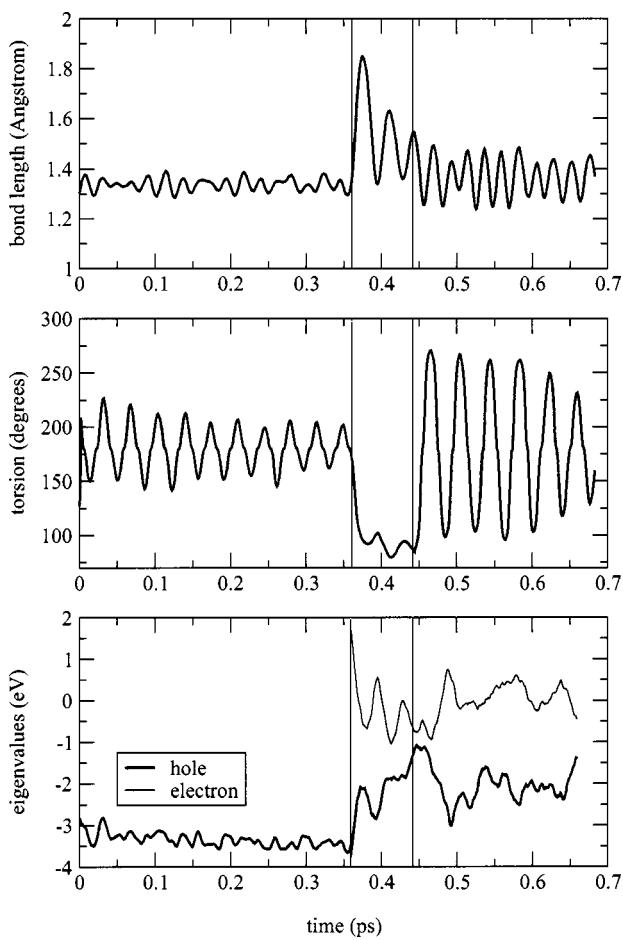


FIG. 4. Top: C=C bond length during the MD run. Middle: H—C=C—H torsion angle. Bottom: KS eigenvalues, the exciton was switched on after $t=0.36$ ps; radiationless recombination takes place at $t=0.44$ ps.

occurs in order to minimize the electrostatic repulsion between the hydrogen atoms [Fig. 3(c)]. The KS eigenvalues as a function of time are shown in Fig. 4. Right after the exciton injection, the electron and hole energy levels moved quickly toward each other at mid gap, reaching a minimal energy difference of 0.7 eV after only 0.084 ps. That we could clearly take as evidence of NREHR; we therefore decided to mimic the actual radiationless recombination by restoring at that moment the occupation numbers and the wave functions on the ground state. The system quickly came back to the initial transconfiguration with large oscillations around 180°. The average overall temperature of the system in the microcanonical ensemble increased by about 150 K due to the energy release.

For a better appraisal of the nature of the trapped $e-h$ state at the vinyl defect, we came back to the distorted excited state structure reached by MD simulation, just before the recombination took place and relaxed statically the atomic positions in order to minimize the zero-temperature total energy. The optimal torsion angle is 84° and the C=C distance is 1.45 Å. The singly-occupied KS orbitals of that state are sketched in Fig. 3(c). From this picture it is evident that the π bond is broken, leaving two singly occupied p_z orbitals on the two carbon atoms; the orbitals are degenerate and the probability of a nonradiative recombination is indeed

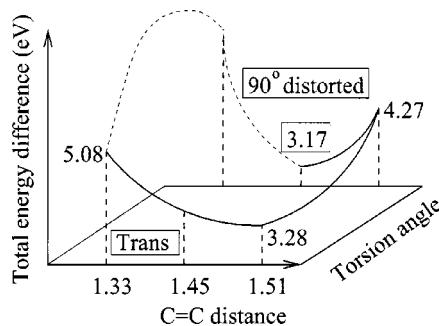


FIG. 5. Potential energy surfaces of the vinyl defect. Total energy differences are calculated respect to the ground state.

very high. Experimentally, it is probable that nonradiative recombination will take place after some lingering at a vinyl defect. However, that event does not appear in our simulation to cause irreversible damage, but simply release energy to phonons.

Summing up the results collected about the vinyl excited state, we were able to sketch potential energy surface the excited state of the vinyl defect (Fig. 5). We note that this electron-hole state trapped at the vinyl defect is remarkably reminiscent of the excited state well-known for the ethylene molecule, shown in Fig. 6.

C. Carboxyl defect

PE-modifying agents containing a carboxyl group ($-COOH$) are widespread in practical applications, because the carboxyl group is more electronegative than the carbonyl group, and will trap electrons in a deeper level than the carbonyl. As a prototype of those chemicals, we studied a simple carboxyl group grafted directly to the PE chain, on top of the surface of a *lamella*, so as to accommodate the carboxyl defect in the empty interlamellar interface space. Figure 7 shows a small portion of such a surface. Our simulation cell contains a single carboxyl group, in a slab geometry, with ≈ 8 Å of vacuum between a lamella and the next.

Following the same procedure as for the previous simulations, we first equilibrated the system by classical MD, and subsequently we carried out an *ab initio* molecular dynamics simulation. The highest occupied molecular orbital of this

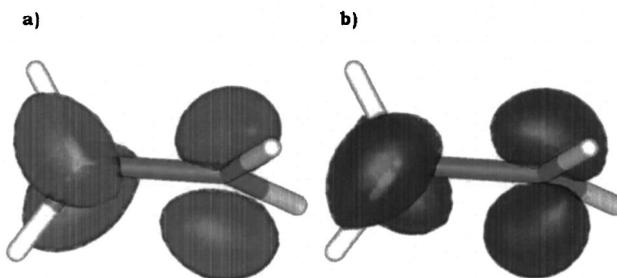


FIG. 6. (a) Hole wave function of the excited ethylene molecule ($[CH_2=CH_2]^*$). (b) Electron wave function orbital. The initial HOMO-LUMO gap in the undistorted geometry is 7.26 eV. The energy difference between the electron and the hole energy level is 0.10 eV.

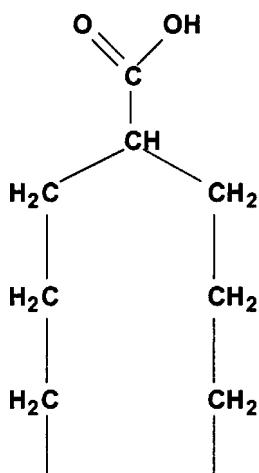


FIG. 7. Schematic drawing of the carboxyl group on top of a lamella.

system prior to excitation is on the oxygen lone pair; the first unoccupied molecular state is a three-center π orbital on the O=C=O atoms (Fig. 9, top).

We performed 0.36 ps of *ab initio* molecular dynamics in the exciton state, during which the carboxyl group started to rotate around the C—C bond that grafts it to the surface. The —COOH group also deviated from planarity, and the carbon atom changed its hybridization, from planar sp^2 to tetrahedral sp^3 . Figure 9 center shows a snapshot of the electron and hole wave functions at the end of the molecular dynamics simulation. The clearest new feature is the electron, now also localized on the C—COOH bond, thus populating the antibonding orbital. As a result one can surmise that the C—COOH bond should have become weaker and if so it could be broken with a relatively low barrier.

In order to estimate the probability of breaking that bond, we performed several molecular dynamics runs, con-

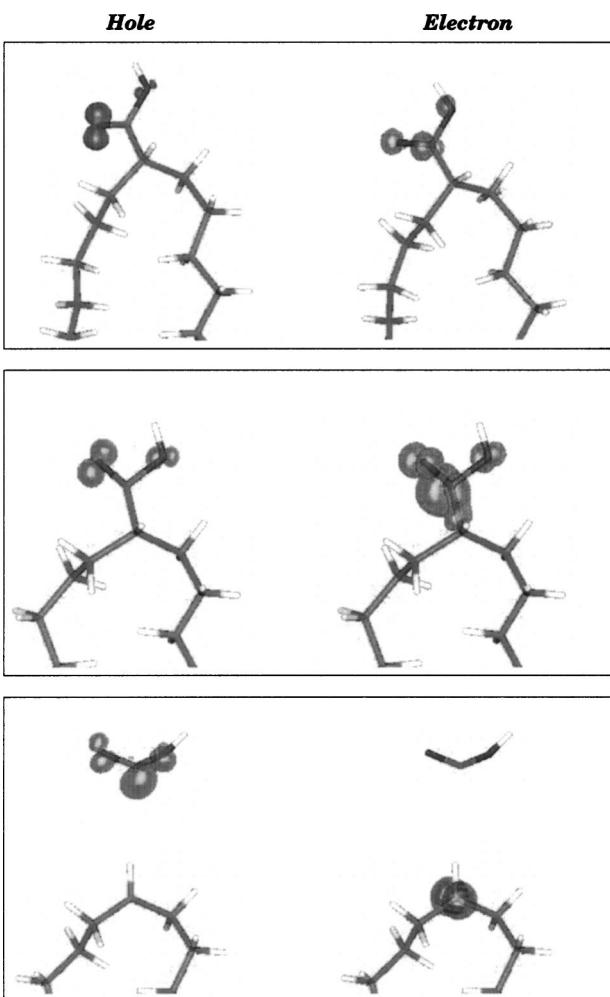


FIG. 9. Top: HOMO and LUMO of the carboxyl group. Center: Electron (right) and hole (left) orbitals at the end of the MD run in the excited state; bottom: electron (right) and hole (left) orbitals of the dissociated system.

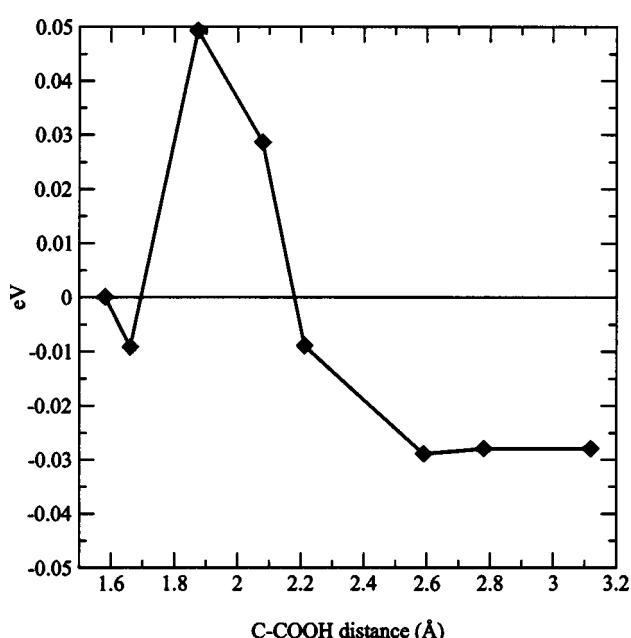


FIG. 8. Total energy of the carboxyl system as a function of the C—COOH bond in angstrom. The barrier is 50 meV high.

straining the C—COOH distance at increasing values. At the end of each MD run, we minimized by the steepest descent the total energy of the structure. The total energy as a function of the C—COOH distance, is shown in Fig. 8. The activation barrier for C—COOH bond breaking is in fact small, about 50 meV in our calculation. In the dissociated state (Fig. 9, bottom), the system is 20 meV lower in energy than the starting state. The dissociated state is made of a dangling bond on the polymeric chain and a carboxyl-radical (COOH^*), which in principle will diffuse away and react with other segments of the chain. A barrier as small as 50 meV can, of course, be overcome thermally with a non-negligible probability in the real system at room temperature. We stress again that our value of the dissociation barrier could be drastically affected by the neglect of spin, in our calculation. We did not investigate alternative paths to NRHER, via two-electron (optically dark) excitations.

We conclude that the carboxyl defect is not only the most efficient at capturing the electron-hole pair, but also one which is dangerously close to a dissociative radiationless recombination, with radicals and broken bonds as by-products. Hence, if not stabilized, it might conceivably act as a germ for electrical damage. On the other hand, a stabilized car-

boxyl group would very securely trap all electrical charge—and possibly all electrically charged migrating molecules at the interface—thus reducing the possibility of damage.

IV. DISCUSSION AND CONCLUSIONS

In conclusion, we found that in presence of common chemical defects, an injected exciton in polyethylene will generally become trapped and may lead to a variety of different outcomes.

Simple trapping without NREHR is possible, as exemplified by the carbonyl defect. In a case like that, the likeliest possibility will be a radiative recombination. By virtue of a large Stokes shift, the emitted photon will fall in the band gap of PE, and therefore will not cause further absorption or damage.

Trapping with NREHR of the nondissociative kind is instead exemplified by the vinyl group. Here, the full exciton energy is suddenly released to the neighboring constituent atoms of PE, resulting in a violent form of local heating. With about 8.8 eV released, and based on a latent heat of melting of 0.032–0.041 eV/formula unit, the radius of the resulting melted region can be estimated in 34 Å.

In a third type of case, the trapped exciton not only leads to NREHR but is also able to weaken some chemical bonds, and can thus lead to a direct form of dissociation, or at least to low-barrier thermal detachment—such as that predicted for the carboxyl group—which may leave the system with some dangerous free radical species. This last class of behavior may represent a likely source of mechanical and electrical damage.

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- ¹L. A. Dissado and J. C. Fothergill, *Electrical Degradation and Breakdown in Polymers* (Peter Peregrinus, Stevenage, UK, 1992).
- ²D. Ceresoli, M. C. Righi, E. Tosatti, S. Scandolo, G. Santoro, and S. Serra, in *Electron-Hole Trapping and Self-Trapping in Polyethylene*, “Festschrift in Honor of F. Bassani”, edited by G. Grossi, G. Larocca, and M. P. Tosi (Scuola Normale Superiore Pisa, 2001).
- ³M. C. Righi, S. Scandolo, S. Serra, S. Iarlori, E. Tosatti, and G. Santoro, *Phys. Rev. Lett.* **87**, 076802 (2001).
- ⁴R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985).
- ⁵P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, 864B (1964); W. Kohn and L. J. Sham, *Phys. Rev.* **140**, 1133A (1965).
- ⁶S. Serra, S. Iarlori, E. Tosatti, S. Scandolo, and G. Santoro, *Chem. Phys. Lett.* **331**, 339 (2000).
- ⁷S. Serra, E. Tosatti, S. Iarlori, S. Scandolo, and G. Santoro, *Phys. Rev. B* **62**, 4389 (2000).
- ⁸S. Serra, E. Tosatti, S. Iarlori, S. Scandolo, and G. Santoro, *Chem. Phys. Lett.* **360**, 487 (2002).
- ⁹A. Becke, *Phys. Rev. A* **38**, 3098 (1988); C. Lee, W. Yang, and R. Parr, *Phys. Rev. B* **37**, 785 (1988).
- ¹⁰N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991).
- ¹¹M. Bernasconi, G. L. Chiarotti, P. Focher, M. Parrinello, and E. Tosatti, *Phys. Rev. Lett.* **78**, 2008 (1997).
- ¹²C. J. Bocchetta, E. Tosatti, and S. Yin, *Z. Phys. B: Condens. Matter* **67**, 89 (1987).
- ¹³M. S. Hybersten and S. G. Louie, *Phys. Rev. B* **34**, 5390 (1986); S. Ismail-Beigi and S. G. Louie, *Phys. Rev. Lett.* **90**, 076401 (2003).
- ¹⁴L. Bernasconi, M. Sprak, and J. Hutter, *J. Chem. Phys.* **119**, 12417 (2003).
- ¹⁵G. Onida, L. Reining, and A. Rubio, *Rev. Mod. Phys.* **74**, 601 (2002).
- ¹⁶I. Frank, J. Hutter, D. Marx, and M. Parrinello, *J. Chem. Phys.* **108**, 4060 (1998).
- ¹⁷F. Bassani and G. Pastori Parravicini, *Electronic States and Optical Transitions in Solids* (Pergamon, Oxford, 1975).
- ¹⁸W. Stier and O. V. Prezhdo, *J. Phys. Chem. B* **106**, 8047 (2002); W. Stier and O. V. Prezhdo, *J. Mol. Struct.: THEOCHEM* **630**, 33 (2003).
- ¹⁹C. F. Jen and A. Warshel, *J. Phys. Chem. A* **103**, 11378 (1999); A. Warshel, *Acc. Chem. Res.* **35**, 385 (2002).
- ²⁰N. L. Allinger, Y. H. Yuh, and J.-H. Lii, *J. Am. Chem. Soc.* **111**, 8551 (1989).