

## Calculation of C 1s core-level shifts in poly(ethylene terephthalate) and comparison with x-ray photoelectron spectroscopy

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Using a first-principle approach, we investigate the C 1s core-level shifts of poly(ethylene terephthalate). The geometrical structure of the polymer is first fully relaxed, then the C 1s core-level shifts are obtained using an approach that includes core-hole relaxation. We compute shifts without geometry relaxation of the excited system, as well as with this relaxation, and find that one of the relative core-level shifts is affected by as much as 0.7 eV by this choice. We compare our *ab initio* core-level shifts with experimental x-ray photoelectron spectroscopy measurements.

### I. INTRODUCTION

Density-functional theory (DFT) has recently been proposed as a tool for computing x-ray photoelectron spectroscopy (XPS) core-level shifts in the case of small organic or inorganic systems.<sup>1–5</sup> Such an accurate theoretical scheme proves useful in this context because a simpler analysis of the experimental core-level shifts often leads to incorrect conclusions for moderately complex systems. Therefore, the availability of an accurate methodology (e.g., including final-state effects) to predict those shifts, applicable to large systems (e.g., polymers or metal/polymer interfaces) is of great importance, especially when unknown surfaces or interfaces are considered.

Pehlke and Scheffler<sup>1</sup> obtained relative core-level shifts thanks to differences in DFT total energies, within a pseudopotential–plane-wave technique, as described later. They used the same technique for the computation of surface core-level shifts of some 4d metals.<sup>2</sup> Pedocchi *et al.*<sup>3</sup> successfully applied an all-electron Gaussian-orbital approach to calculate the shifts in the carbon binding energies for a series of molecules. Later, Pasquarello *et al.*<sup>4</sup> extended the use of DFT for the computation of Si 2p core-level shifts at Si-SiO<sub>2</sub> interfaces. They also found a good overall agreement between theory and experiment with an error of less than 3%. More recently, Rignanese *et al.*<sup>5</sup> used a similar approach to study nitrogen incorporation at the Si(001)-SiO<sub>2</sub> interface by evaluating the N 1s core-level shifts for several model systems of the above interface. Their study highlights the crucial role of core-hole relaxation and, to a lesser extent, second-nearest-neighbor interactions.

In this paper we apply the methodology proposed by Pehlke and Scheffler<sup>1</sup> to a larger system, specifically poly(ethylene terephthalate). We determine the relative C 1s binding energy with respect to a reference configuration by making use of a pseudopotential that simulates the presence

of a screened hole in the core of the atom for which the shift is desired. Further, we demonstrate the applicability of Vanderbilt ultrasoft pseudopotentials<sup>6</sup> to the calculation of C 1s core-level binding-energy shifts. The fact that the ultrasoft-pseudopotential scheme allows one to treat rather localized orbitals with a small plane-wave cutoff, combined with the fact that the pseudopotential approach does not treat core states explicitly, allows for the treatment of large systems with only rather modest computational demands. To perform our study, the molecular structure of the polymer is first fully relaxed, and then C 1s core-level shifts (including core-hole relaxation) are calculated using the Vanderbilt ultrasoft-pseudopotential scheme. Finally, the theoretical results are compared with experimental x-ray photoelectron spectroscopy (XPS) data.

### II. THEORETICAL

#### A. Geometry

The poly(ethylene terephthalate) (PET) polymer that is the subject of the present study is shown schematically in Fig. 1. The monomer consists of ten carbon, four oxygen, and eight hydrogen atoms forming a short aliphatic chain (the ethylene segment), as well as an aromatic ring and an ester function that together form the terephthalate group. The model geometry that we have selected for study is shown in Fig. 2.<sup>7,8</sup> It is planar (except for the hydrogen atoms on the aliphatic chain, all atoms are in a plane) with a transconfor-

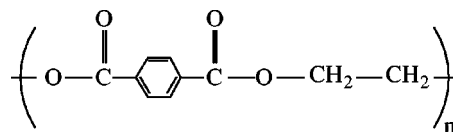


FIG. 1. Molecular structure of the poly(ethylene terephthalate) (PET) repeat unit.

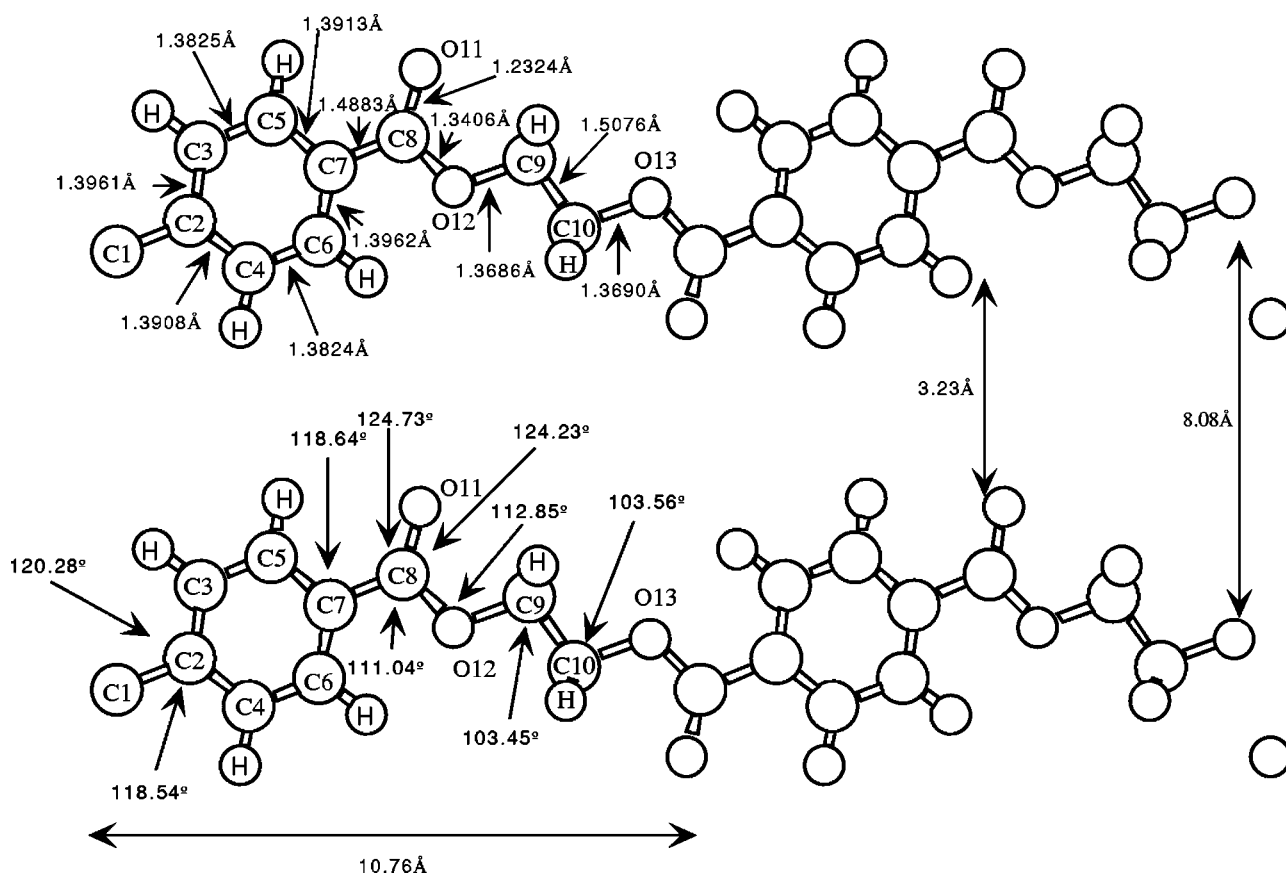


FIG. 2. Molecular and optimized geometric structure of the poly(ethylene terephthalate) (PET) repeat unit.

mation of the oxygen atoms in the glycol segment. In this configuration, the C=O groups are alternately distributed on each side of the polymer backbone. The bond lengths and bond angles, fully optimized in the framework of density-functional theory (DFT) within the local-density approximation (LDA) (see Sec. II B), are also displayed in Fig. 2. Interactions between neighboring chains (along the  $y$  and  $z$  directions) could be neglected thanks to the creation of an interchain vacuum region  $\sim 3.2$  Å wide.

### B. Methodology

For the relaxed structure of PET, the relative core-level shifts were deduced following the method discussed in Ref. 1. Briefly, this technique consists in performing two separate calculations. First, we calculate the total energy of a system [ $E_{ref}^{C=O}$ ] in which the pseudopotential (PP) of a particular C atom, for instance C=O, is replaced by another PP that simulates the presence of a screened core hole in its core. We will refer to the energy characteristic of that calculation as being the reference. Then, a second calculation, involving the replacement of another C atom (for which the shift in core-level binding energy is desired) is undertaken following the same procedure, giving another total energy ( $E_i$ ). The desired core-level shift relative to the reference C is then given by

$$\Delta_i = E_i - E_{ref}^{C=O}. \quad (2.1)$$

In both cases, the computation is carried out in the presence of a negative background to satisfy the charge neutrality requirement. Because both C atoms belong to the same molecule, determining the electronic ground state of the system with a regular PP for all C atoms is unnecessary. In what follows, we will use a notation in which the C atom whose core electron has been removed is underlined: e.g., the reference energy is  $E_i - E_{ref}^{C=O}$ .

Such a calculation entails a certain number of assumptions. In our study, electrons are relaxed to screen the core hole and we assume that the use of a modified PP can be restricted to only those atoms whose core states energies are to be calculated. Regarding the geometrical relaxation, we first evaluate the core-level shifts under the assumption that the molecular structure is the same in the initial and final states (vertical transition). Then, we perform another set of calculations in which we allow the atoms to adapt adiabatically to the photoexcitation: the geometry of the polymer is fully relaxed after photoexcitation (i.e., using the modified PP for the  $\underline{C}$  atom) prior to the shift evaluation. In the remainder of this paper, we present results related to both cases. Finally, we found no effect on the computed core-level shifts when doubling the size of the unit cell, so we can be confident that our results are converged with respect to the supercell size.

For reasons of convenience, the PET atomic relaxation was carried out in the framework of DFT as implemented in the ABINIT code,<sup>9</sup> while the core-level shift calculation was performed using DFT as implemented in the Cusp code.<sup>10</sup>

The latter use a conjugate-gradient technique<sup>11</sup> to minimize directly the Kohn-Sham total-energy functional. In both cases, the core electrons are frozen and for a given geometry of the ions, only the valence electrons are explicitly considered using pseudopotentials (PP's) to account for core-valence interactions.<sup>12</sup> For the structural relaxation, norm-conserving PP's are used for all atoms whereas for the core-level shifts calculations, atoms are described by Vanderbilt ultrasoft PP's. The exchange and correlation energy was evaluated within the local-density approximation (LDA) in the Ceperley-Alder form.<sup>13</sup> The Brillouin zone was sampled using the  $\Gamma$  point. The wave functions were expanded on plane-wave bases defined by cutoffs of 18 hartree (1 hartree = 27.211 eV) for the structural optimization and 12.5 hartree for the core-level shift calculation. For the structural optimizations, the forces on each ion were relaxed to less than  $10^{-2}$  eV/Å using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm.<sup>14</sup>

### III. EXPERIMENT

#### A. Sample

12- $\mu$ m-thick, biaxially stretched semicrystalline poly(ethylene terephthalate) (PET) films (Mylar, Du Pont de Nemours-Luxembourg) were used as substrates. Samples of 1 cm<sup>2</sup> were fixed on the sample holder by means of a double-sided tape and analyzed without further treatment.

#### B. X-ray photoelectron spectroscopy—XPS analysis

XPS measurements were carried out at room temperature in a Kratos XSAM 800 surface analysis system (usual operating pressure during rapid sample introduction and measurement was  $\sim 10^{-8}$  Torr), equipped with a dual anode (Mg/Al) x-ray source and a 100-mm radius concentric hemispherical analyzer. In our study the XPS core-level spectra were recorded using unmonochromatized Mg  $K\alpha$  radiation (1254 eV). The pass energy was 80 eV for the survey spectra and 20 V for the high-resolution studies. The build-up of positive charge occurring on the polymer surface was neutralized by using an electron floodgun. The floodgun was tuned to set the main C 1s component at 285.1 eV binding energy. Under typical working conditions the floodgun electron kinetic energy was set to 10 eV.

Analysis of the XPS spectra included a background subtraction and line-shape decomposition based on Gaussian functions. The data fitting was performed by using minimization criteria based on the  $\chi^2$  method.

### IV. RESULTS

#### A. Initial geometry of PET

The atomic coordinates of the representative structure of the polymer (Fig. 2) were fully relaxed using a periodically repeated unit cell of dimensions  $10.76 \times 8.07 \times 8.07$  Å<sup>3</sup>. The results of the BFGS geometry optimization are presented in Fig. 2. The results show that the structure reproduces quite well the chemical heterogeneity of the polymer. Indeed, the carbon-oxygen bond lengths inside the ester function (O=C—O) are accurately reproduced:<sup>15</sup> the C<sub>8</sub>=O<sub>11</sub> bond length is found to be 1.23 Å whereas the corresponding val-

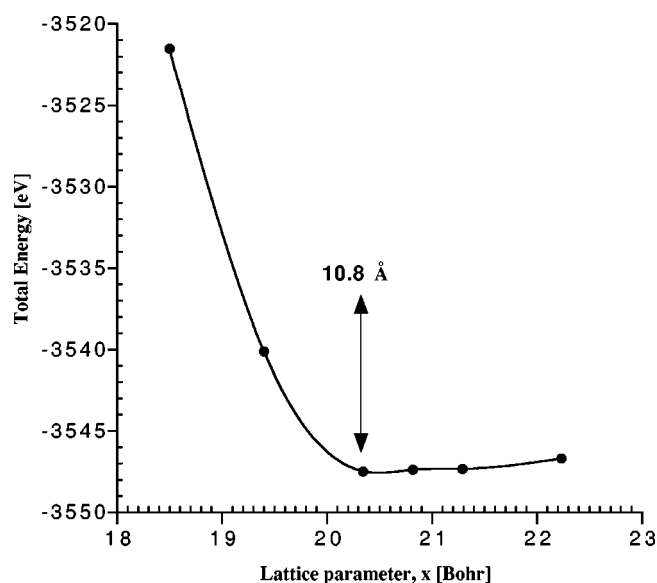


FIG. 3. Determination of the optimized lattice constant of the poly(ethylene terephthalate) (PET) repeat unit along the polymer backbone.

ues for the C<sub>8</sub>—O<sub>12</sub> and O<sub>12</sub>—C<sub>9</sub> bonds are, respectively, 1.34 and 1.36 Å, characteristic of single bonds. In Ref. 14 it is reported that the length of a double C=O bond ranges from 1.19–1.26 Å and the length of a single C—O bond is typically between 1.26–1.37 Å. Our computed values for bond angles inside the ester group are also found to be in good agreement with the data reported in Ref. 14. The phenyl ring and the ester groups are linked to each other through a single carbon-carbon bond of length  $L(\text{C-C}) \sim 1.49$  Å. Again, it is interesting to compare this value with the one reported in Ref. 14 (the length of a single C-C bond is 1.49 Å) or with the one obtained by Calderone *et al.*<sup>16</sup> (1.50 Å) in the case of an acetoxyethylmethylterephthalate (AEMT) molecule. The bond lengths inside the cycle are indicative of its aromatic character, e.g., all C-C bond lengths are about 1.39 Å long. Finally, the ester function and the aliphatic segment are linked to each other through single C-O [O<sub>12</sub>—C<sub>9</sub>, C<sub>10</sub>—O<sub>13</sub>] bonds. Inside the aliphatic chain, the C-C bond displays a single bond character ( $\sim 1.50$  Å).

The lattice parameter along the polymer chain ( $x$  direction) was also fully optimized. The results are presented in Fig. 3. Its equilibrium value is determined as the one which minimizes the total energy. We deduce for the equilibrium lattice parameter a value of  $\sim 10.8$  Å.

#### B. Core-level shifts in PET

Figure 4 summarizes the calculated C 1s shifts for the PET configuration under the assumption that the molecular structure is the same in the initial and final states (vertical transition). As already mentioned, the shifts are given with respect to the binding energy of the carbon involved in the C=O bond. Positive values of the calculated shift correspond to lower binding energies.

The results provide evidence for three distinct groups of C atoms. Group I, which constitutes the reference group, in-

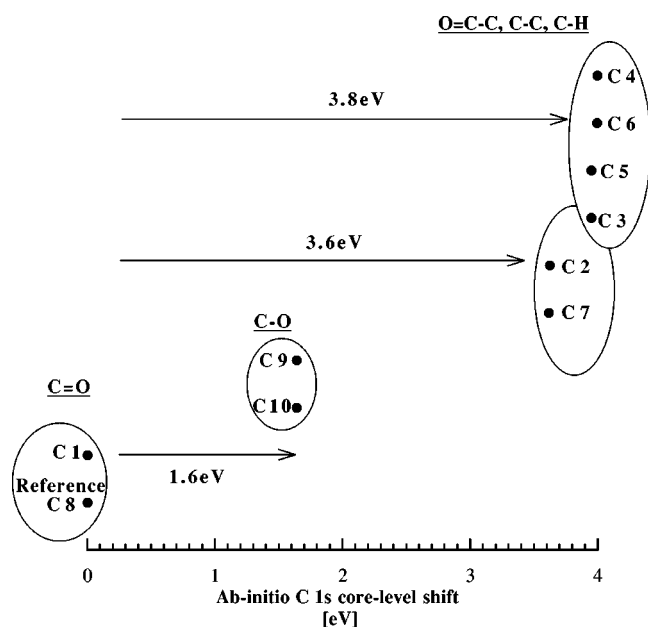


FIG. 4. Relative C 1s core-level shifts of PET under the assumption that the geometries of initial and final states are the same. The shifts expressed in (eV) are given with respect to  $\underline{\text{C}}=\text{O}$ .

volves the two C atoms of the  $\text{O}-\underline{\text{C}}=\text{O}$  functionality. Group II is shifted by  $\sim 1.6$  eV with respect to group I, and corresponds to the two carbons that belong to the  $\text{C}-\text{C}-\text{O}$  segment in which the C atom is single bonded to its O neighbor. In group III, the core-level binding-energy shift ranges from 3.6 to 3.8 eV. This last group can be divided into two subcategories. The first one, which gives a shift of about  $\sim 3.6$  eV with respect to group I, is attributed to the carbon atoms of the phenyl ring ( $\text{O}=\text{C}-\underline{\text{C}}-\text{C}$ ) having a highly electronegative O of the  $\text{C}=\text{O}$  bond as a second neighbor (i.e., directly connected to the ester functionality). The second one, for which the relative binding energies are  $\sim 3.8$  eV with respect to group I, is related to the four remaining C atoms that belong to the aromatic ring. We therefore estimate that the presence of a highly electronegative double-bonded O as a second neighbor induces a shift of about 0.2 eV.

A geometry optimization was performed for each of the previously discussed cases after the replacement of the modified PP and prior to the evaluation of the core-level shifts. Table I illustrates the changes in bond lengths and bond angles when the regular PP of a given carbon atom is re-

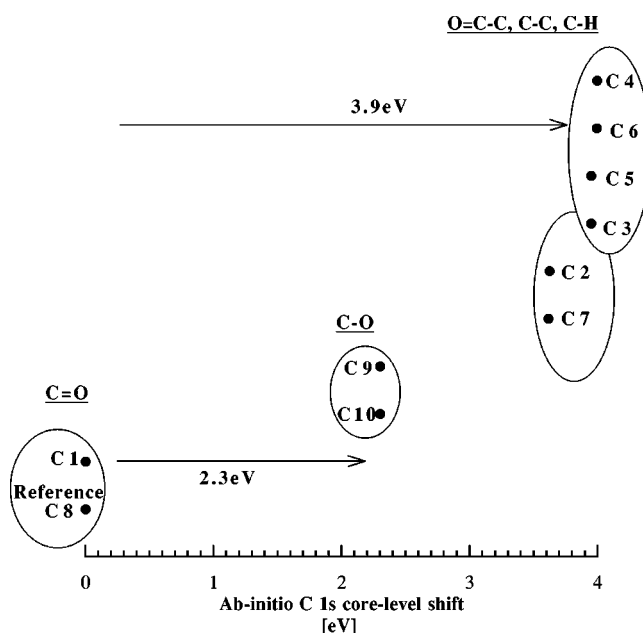


FIG. 5. Relative C 1s core-level shifts of PET under the assumption that the geometries of initial and final states are different. The shifts expressed in (eV) are given with respect to  $\underline{\text{C}}=\text{O}$ .

placed by the modified PP. As a general trend, we observe that the bond angle values fluctuate by approximately 1% to 4% with respect to the values inside the polymer prior to photoexcitation (initial state). The table shows that these fluctuations in the geometrical parameters (bond lengths and bond angles) affect mostly the ester and ethylene parts of the molecule. As result of these fluctuations, the calculated (adiabatic) core-level shifts, presented in Fig. 5, are found to be 2.3 eV (between groups I and II) and 3.9 eV (between group I and III). It is seen that the shifts between the core-level binding energies of the  $\underline{\text{C}}-\text{O}$  and  $\underline{\text{C}}=\text{O}$  are much more sensitive to the geometry of the polymer as compared to the one between the  $\underline{\text{C}}-\text{C}/\underline{\text{C}}-\text{H}$  and the  $\underline{\text{C}}=\text{O}$ .

## V. DISCUSSION—COMPARISON WITH EXPERIMENT

Based on the polymer chemistry, the two C atoms involved in the  $\underline{\text{C}}=\text{O}$  bonds are expected to be characterized by higher binding energies because of their highly electronegative chemical environment. We also expect the six C atoms involved in the  $\underline{\text{C}}-\text{C}$  and  $\underline{\text{C}}-\text{H}$  bonds inside the phenyl ring to appear at the lowest binding energy, due to the

TABLE I. Final-state effects on the geometrical parameters of PET. A geometry optimization is performed after the replacement of the modified PP and prior to the evaluation of the core-level shifts. The results of the geometry optimizations are presented for a few selected cases.

Angle	Initial	$\underline{\text{C}}_1$	$\underline{\text{C}}_2$	$\underline{\text{C}}_6$	$\underline{\text{C}}_9$	$\underline{\text{C}}_{10}$
$\text{C}_7-\text{C}_8-\text{O}_{11}$	124.73	123.51	122.72	120.83	125.85	133.21
$\text{O}_{11}-\text{C}_8-\text{O}_{12}$	124.24	124.17	125.42	129.21	121.73	119.40
$\text{C}_7-\text{C}_8-\text{O}_{12}$	111.03	112.31	111.86	109.97	112.42	107.39
$\text{C}_8-\text{O}_{12}-\text{C}_9$	112.82	111.20	113.20	114.22	108.27	105.43
$\text{O}_{12}-\text{C}_9-\text{C}_{10}$	103.50	102.41	102.86	101.08	102.73	105.58
$\text{C}_9-\text{C}_{10}-\text{O}_{13}$	103.55	102.10	103.10	104.59	105.59	102.70



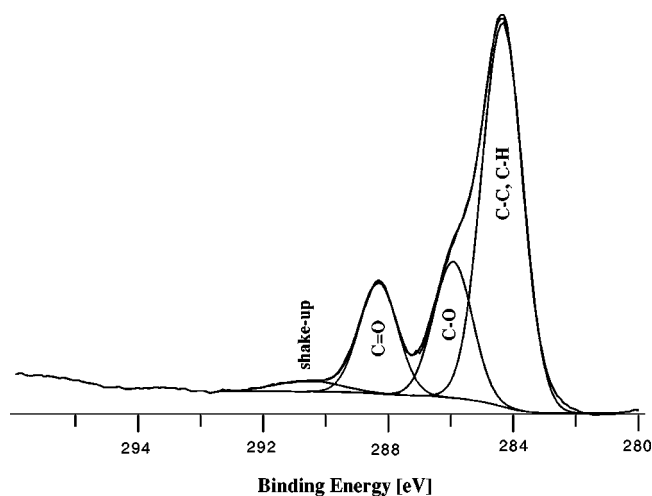


FIG. 6. XPS C 1s spectrum of PET.

presence of a “neutral” chemical environment. Finally, we expect the two C atoms of the  $\text{C}-\text{O}$  bond to appear at intermediate binding energies.

Figure 6 shows the C 1s XPS spectrum of the PET film. On the basis of the considerations of the previous paragraph, we used four different contributions to fit the C 1s peak. The low binding-energy peak, centered at 285 eV, is resolved into two components (one for  $\text{C}-\text{C}$  and  $\text{C}-\text{H}$ , the other for  $\text{C}-\text{O}$ , while the high binding-energy peak, located at  $\sim 288.3$  eV, is attributed to the doubly bonded C of the ester function ( $\text{O}=\text{C}-\text{O}$ ). The ratio between the intensities of these three components is approximately 3:1:1 as expected from the polymer stoichiometry. Finally, a fourth component associated with shake-up processes is centered at  $\sim 290.8$  eV. The relative binding-energy shift between component 1 ( $\text{C}-\text{C}, \text{C}-\text{H}$ ) and component 3 ( $\text{C}=\text{O}$ ) is found to be 4 eV, whereas that between component 2 ( $\text{C}-\text{O}$ ) and component 3 is about 2.4 eV. These values are in good agreement with those obtained previously by other groups<sup>16,17</sup> (4 eV between components 1 and 3, and 2.5 eV between components 2 and 3).

Because of the short-time scale of photoelectron emission, one normally assumes that the geometries in both the initial and final states are identical. Under this assumption, we found that the calculated core-level shift of the  $\text{C}-\text{O}$  component with respect to the  $\text{C}=\text{O}$  is underestimated by about 30% as compared to its experimental value. Surprisingly, we find that the discrepancy with experiment regarding this shift is almost entirely removed if we allow for structural relaxation in the final state (i.e., in the presence of the core hole). On the other hand, the shift between group I and group III transitions appears to be less sensitive ( $\sim 0.1$  eV) to the geometry of the final state.

The inclusion of the final-state structural relaxations is clearly problematic. On the one hand, our calculations give an unambiguous prediction of the structural relaxations that would occur in the presence of the core hole; these are typically  $\sim 1\%$  to  $4\%$  with respect to the initial configuration, and occur mainly in the ester/ethylene parts of the molecule. If these relaxations are included in the core-level shift calculations, we find greatly improved agreement with experiment. On the other hand, there are strong theoretical reasons

to expect that the photoemission process occurs on a time scale that is too short to allow such structural relaxation. If it is included, our methodology leads to a global underestimation of the shifts by about  $\sim 0.1$  eV in the best case.

Thus, it is important to look for other possible sources of error in the theoretical calculations. We carried out several checks to test whether our calculations are converged for the model system that we considered, namely, an isolated polymer chain. For example, under the assumption that the atomic geometries are the same in the initial and final states, we varied the interchain distance in the  $y$  direction but found no effect on the core-level shifts values. We also doubled the size of the unit cell in the  $x$  direction to see how the presence of a negative background could affect our data, and again, found no effect on the computed core-level shifts. The adjustment of the interchain distance in the  $z$  direction, which could affect the interaction between the delocalized electrons of the benzene rings, was not as carefully tested. However, the real experimental system is not composed of isolated chains, and it could be that the interchain interactions in the real polymer might modify the core-level shifts significantly, for example by providing a modified screening environment.

Also, it is difficult to estimate the inherent errors in the core-level shifts associated with the use of our basic approximation, the LDA approach to DFT. In particular, any independent-particle theory of the excitation process is unable to account for correlation effects beyond a mean-field level, although they are at the origin of the shake-up feature seen in the spectrum. These correlation effects might also affect the magnitudes of the core-level shifts to some degree. Pedocchi *et al.*<sup>3</sup> investigated different approximations to DFT: the local-density approximation, as well as a nonlocal (generalized gradient) approximation. They found that the relative core-level shift errors in the LDA ranged between 0.1 and 0.8 eV, and were somehow reduced within the generalized-gradient approximation. They also compared adiabatic versus vertical transitions for four small molecules with  $\text{C}-\text{H}$ ,  $\text{C}=\text{C}$  and  $\text{C}=\text{O}$  bonds. For these, relaxation effects on the relative core-level shifts were always less than 0.1 eV. This is in contrast with our finding of a large relative shift between  $\text{C}-\text{O}$  and  $\text{C}=\text{O}$  in an extended system.

Further studies of molecules that show a large relaxation effect on relative core-level shifts are needed to assess whether the better agreement observed here for adiabatic shifts is due to a fortuitous cancellation of errors, or whether special circumstances weaken the previously mentioned theoretical reason against the inclusion of the relaxation effect.

## VI. CONCLUSION

We successfully applied density-functional theory to predict the core-level shifts in the case of large molecules (i.e., polymers). We found an overall good agreement between theory and experiment if both electronic and structural relaxation are carried out after photoexcitation. However, if only electronic relaxation is considered, assuming that the ejection of a photoelectron leaves the geometrical structure of the polymer intact, we find a less satisfactory agreement with respect to the experimental measurements of the C 1s core-level shifts.

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- <sup>1</sup>E. Pehlke and M. Scheffler, Phys. Rev. Lett. **71**, 2338 (1993).  
<sup>2</sup>J.N. Andersen, D. Hennig, E. Lundgren, M. Methfessel, R. Nyholm, and M. Scheffler, Phys. Rev. B **50**, 17 525 (1994).  
<sup>3</sup>L. Pedocchi, N. Russo, and D.R. Salahub, Phys. Rev. B **47**, 12 992 (1993).  
<sup>4</sup>A. Pasquarello, M.S. Hybertsen, and R. Car, Phys. Scr. **T66**, 118 (1996); A. Pasquarello, M.S. Hybertsen, and R. Car, Phys. Rev. B **53**, 10 942 (1996).  
<sup>5</sup>G.-M. Rignanese, A. Pasquarello, J.-C. Charlier, X. Gonze, and R. Car, Phys. Rev. Lett. **79**, 5174 (1997).  
<sup>6</sup>D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).  
<sup>7</sup>Y. Travaly, P. Bertrand, G.-M. Rignanese, and X. Gonze, J. Adhes. **66**, 339 (1998).  
<sup>8</sup>Y. Travaly, P. Bertrand, X. Gonze, and G. -M. Rignanese, in *Polymer-Solid Interfaces: from Model to Real Systems*, edited by J.J. Pireaux, J. Delhalle, and P. Rudolf, *Proceedings of the Second International Conference, Namur, 1996* (Presses Universitaires de Namur, Namur, Belgium, 1997), pp. 453–465.  
<sup>9</sup>The ABINIT code is a common project of the Catholic University of Louvain, Corning Inc., and other contributors (URL://www.pcpm.ucl.ac.be/abinit). The electronic ground state is found thanks to a combination of a non-self-consistent state-by-state gradient algorithm, see Ref. 11, and a potential-based conjugate gradient algorithm [X. Gonze, Phys. Rev. B **54**, 4383 (1996)]; An efficient fast-Fourier transform implementation is also used [S. Goedecker, SIAM J. Sci. Comput. **1**, 1605 (1997)].  
<sup>10</sup>R.D. King-Smith and D. Vanderbilt, Phys. Rev. B **49**, 5828 (1994).  
<sup>11</sup>M.C. Payne, M.P. Teter, D.C. Allan, T.A. Arias, and J.D. Joannopoulos, Rev. Mod. Phys. **64**, 1045 (1992).  
<sup>12</sup>W. Kohn and L. Sham, Phys. Rev. A **140**, 1133 (1965).  
<sup>13</sup>D.M. Ceperley and B.J. Adler, Phys. Rev. Lett. **45**, 566 (1980).  
<sup>14</sup>W.H. Press, B.P. Flannery, S.A. Teukolsky, and W.T. Vetterling, *Numerical Recipes: The Art of Scientific Computing* (Cambridge University Press, Cambridge, England, 1989).  
<sup>15</sup>See, for example, *The Chemistry of Carboxylic Acids and Ester*, edited by S. Patai (Interscience, New York, 1969).  
<sup>16</sup>A. Calderone, R. Lazzaroni, J.L. Bredas, Q.T. Le, and J.J. Pireaux, J. Chem. Phys. **102**, 4299 (1995).  
<sup>17</sup>M. Bou, J.M. Martin, Th. Le Mogne, and L. Vovelle, Appl. Surf. Sci. **47**, 149 (1991).