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A poly-epoxy surface explored by Hartree-Fock ΔSCF simulations of C1s XPS spectra

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Whereas poly-epoxy polymers represent a class of materials with a wide range of applications, the structural disorder makes them difficult to model. In the present work, we use good experimental model samples in the sense that they are pure, fully polymerized, flat and smooth, defect-free, and suitable for ultrahigh vacuum x-ray photoelectron spectroscopy, XPS, experiments. In parallel, we perform Hartree-Fock, HF, calculations of the binding energies, BEs, of the C1s electrons in a model molecule composed of the two constituents of the poly-epoxy sample. These C1s BEs were determined using the HF ΔSCF method, which is known to yield accurate values, especially for the shifts of the BEs, ΔBEs. We demonstrate the benefits of combining rigorous theory with careful XPS measurements in order to obtain correct assignments of the C1s XPS spectra of the polymer sample. Both the relative binding energies—by the ΔSCF method—and relative intensities—in the sudden approximation, SA, are calculated. It results in an excellent match with the experimental spectra. We are able to identify 9 different chemical environments under the C1s peak, where an exclusively experimental work would have found only 3 contributions. In addition, we observe that some contributions are localized at discrete binding energies, whereas others allow a much wider range because of the variation of their second neighbor bound polarization. Therefore, HF-ΔSCF simulations significantly increase the spectral resolution of XPS and thus offer a new avenue for the exploration of the surface of polymers. [http://dx.doi.org/10.1063/1.4960762]

I. INTRODUCTION

The reactivity of poly-epoxy surfaces is of major concern regarding functionalization pretreatments or treatments. The lack of simulations and models is an obstacle for efficient technology developments which, nowadays, rely exclusively on empirical studies. A good illustration can be found in the field of metallization of poly-epoxies and adhesion of metallic films in the sample list in Ref. 1. Therefore, the development of an accurate model for the surface of poly-epoxies can help in the design of tailored surfaces with a good control of the chemical reactivity. While the family of poly-epoxy materials is strategic in many industrial applications, there have, until now, been very few attempts to develop accurate and reliable models on their surfaces or interfaces with other materials.[2,3]

X-ray photoelectron spectroscopy, XPS, is an excellent experimental technique for assessing the composition and also the properties of the polymer surface, especially when the shifts of core-level binding energies, ΔBEs, can be interpreted in terms of the electronic structure of the polymer.[4] In particular, we show in this paper that the information gained from XPS studies could be a powerful tool to assess the reactivity of polymer surfaces. The XPS 1s binding energies, BEs, of carbon, nitrogen, and oxygen atoms are good probes of the structure of the polymer because they are sensitive to the environment of the core-ionized atom. This is particularly important since it is often possible to have an unambiguous resolution, or decomposition, of the XPS 1s spectra into contributions from one or from a few atoms in different functional units. However, in order to draw correct inferences about the polymer structure, it is necessary to have definitive assignments of the various BEs to their origins in the different inequivalent atoms in the polymer. The simulation of the XPS spectra based on rigorous and accurate *ab initio* Hartree-Fock, HF, calculations provides theoretical support for making such definitive assignments. Thus, it represents an important step in our goal of better understanding the character of poly-epoxy surfaces.

To our knowledge, there is no model for polymer surfaces but rather models derived from calculations on model molecules. For instance, polymers[5–9] and related organic materials[10] have all been modeled from the properties of one or a few constituent molecules. The numerous studies using this method prove statistically that such an approximation is globally correct. Some authors have tried to go a step beyond and dealt with the calculations of the adsorption of atoms or molecular species on these model molecules, e.g., in the study of the adsorption of Al on polyethylene terephthalate (PET).[11]

The interpretation of XPS spectra of a wide range of materials based on rigorous calculations of the electronic wavefunctions of the materials has been studied extensively;

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see, for example, the recent review of Bagus *et al.*[4] In the present paper, we will use the HF, ΔSCF method where the BEs are taken as the difference in the HF self-consistent field, SCF, energies of the ground state (GS) and the core-ionized state.[4] The ΔSCF method includes the initial state contributions due to the charge distribution in the ground state and the final state contributions due to the electronic relaxation in response to the core-hole. It is necessary to include the final state effects since the relaxation may be different for the ionization of different inequivalent atoms.[12] The accuracy of the HF ΔSCF method is adequate for our purposes. This adequacy has been documented in the review of Ref. 4 and in three recent papers,[12–14] where the XPS BEs have been studied for a large number of molecules containing C, N, and O atoms. In these latter works,[12–14] HF and density functional theory, DFT, BEs, and BE shifts, ΔBEs, have been compared to experimental data. For the HF ΔSCF results, the C1s, N1s, and O1s BEs of these molecules have an absolute accuracy of ~1 eV but, most important for our purposes, the error of the ΔBEs, between an atom in different molecules or in different environments is much smaller, ~0.2 eV.[12–14] In this context, it is worth noting that, especially for insulating surfaces, it may be difficult to determine an absolute value of the BEs with respect to vacuum zero of energy,[4,15] but it is straightforward to obtain accurate shifts of the BEs for different atoms in the same material. For this reason, the focus of our discussion will be concerned with the ΔBE. Furthermore, our concern is for the main 1s peaks and we do not focus on the shake satellites that steal intensity from these main peaks.[16–18] However, it is necessary to consider the losses to shake peaks in determining the main peak intensities, since these losses may not be the same for all inequivalent atoms; in other words, the relative intensities of the 1s BEs of inequivalent atoms are not exactly given by the stoichiometry of the compound.[19] An advantage of using HF wavefunctions is that they provide a natural way to determine the relative intensities, I_{rel}, of the main 1s peaks. These I_{rel} are discussed in more detail later in the paper.

It is appropriate to note that there have been recent work where the interpretations of the N(1s)[20] and the C(1s)[21] XPS spectra of organic molecules that involve only the use of the electronic structure of the initial configuration as given by DFT[20,21] and by Moller-Plesset perturbation theory.[21] On the other hand, the separate calculation of wavefunctions for both the initial and final, core-hole, configurations is required with the ΔSCF method that we have used. This one configuration approach is described as being in the spirit of Koopmans' theorem[20,21] and has the computational advantage that only a single electronic structure DFT calculation is needed. However, this approach neglects final state relaxation.[4] For the BEs, the only important concern is for the differential relaxation energies of the XPS BEs of interest since the main concern in the present and in the prior work[20,21] is for BE shifts, ΔBE. For the N(1s) BEs of 15 molecules,[12,14] the relaxation energies differed by 1.7 eV, for HF, and 1.8 eV, for DFT, between the largest and smallest relaxation energies. For the molecules used in our models, this differential relaxation was somewhat smaller, 1.1 eV, but still large enough to be of concern for the analysis of the spectra. It is possible, as pointed out in Refs. 20 and 21, to make adjustments to partially account for these differential relaxation effects, but the adjustment parameters limit the *ab initio* character of the theoretical analysis. Another factor that is missing in Koopmans' theorem approach is differential losses to shake satellites for the different C(1s) ionizations in the model dimer. Of course, these losses to shake satellites are at the expense of intensity that appears in the main peak.[17,18] For our model dimer, these losses range between a smallest loss of 25% to a largest loss of 35%. Neglecting these differential losses, which we take fully into account, introduces an uncertainty of ~15% in the intensity assignments and in the theoretical modelling of the XPS spectra. An important computational reason for avoiding calculation for the final states is the difficulty of convergence to electronic structure of the hole-state configurations in a complex molecule. However, as we will discuss in Sec. II, we have developed a methodology that avoids the convergence problems and makes the calculation of the final, hole-state, electronic structure routine and automatic. Given this development in methodology, we feel that it is worth carrying out ΔSCF calculations to avoid the uncertainties of the Koopmans' theorem approach that we have described above.

For our XPS studies of the origins of the C(1s) ΔBEs, we have chosen to study a model molecule as representative of the poly-epoxy used in the XPS experiments. We choose a poly-epoxy polymer that is synthesized in such conditions that its surface is smooth, its chemical composition is homogeneous and that it is fully polymerized. Details about synthesis and surface characterizations can be found elsewhere.[3]

Whereas it is experimentally obtained from the stoichiometric mixture of 2 DGEBA + 1 ethylene diamine (EDA), the model molecule consists in a dimer of 1 diglycidylether of bisphenol A (DGEBA) + 1 EDA, as shown in Fig. 1. Hence, the model contains all the possible bonds in the solid surface while minimizing the number of atoms (61 including the H atoms). ΔSCF calculations are performed at the HF level and, hence, include fully the final state relaxation of the electronic wavefunction in response to the core-hole. There have been previous calculations of the core-level spectra of large molecules; see, for example, Refs. 22–24. However, the present case is somewhat special in that the molecular model that we use has no symmetry and, in consequence, we have had to determine the wavefunctions for 29 distinct and different C1s core-hole states as well as the wavefunction for the ground state.

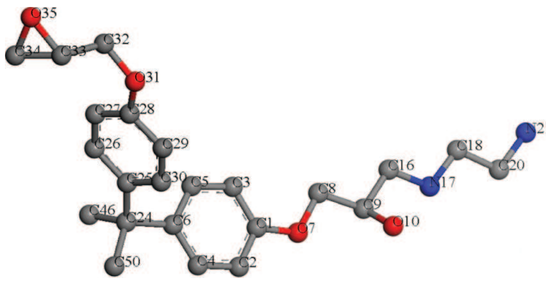

FIG. 1. Model dimer made of 1 diglycidylether of bisphenol A (DGEBA) and 1 ethylene diamine (EDA) molecules, through the reaction of one NH_2 proton of EDA that opens one epoxy ring of DGEBA. H atoms are not shown for clarity.

The paper is organized as follows. Experiments and calculation details are presented. Then, we present ΔSCF results from HF calculations for both binding energy shifts and intensities derived from the sudden approximation[17,18] and show the advantages of such a careful analysis in contrast with an "empirical" decomposition of the XPS spectra. Finally, results are discussed and emphasis is placed on the need to extend our present strategy.

II. COMPUTATION AND THEORETICAL DETAILS

We use the model molecule shown in Fig. 1, which geometry was optimized at the B88PW91/TZVP level of theory using the DeMon2k software.[25]

For this large system, we made these initial HF calculations with a modest basis set that is slightly more extended that double zeta, DZ+; see, for example, Ref. 26. The basis set is made with contracted Cartesian Gaussian functions. For the C, N, and O atoms, the basis set was based on the 9s and 5p basis set of van Djinevelt[27] contracted to 4s and 3p functions, (9,5/4,3). For the H atoms, the basis set was (4,1/2,1) where the s basis function exponents were taken from van Djineveldt[27] supplemented by a p function with exponent 1.0. Calculations of Hartree-Fock wavefunctions for the ground state of the molecule and for configurations where the 1s shell of each of the C atoms was singly occupied. Convergence to the hole-states where the singly occupied orbital had the proper localized 1s character was assured by selecting the occupied orbitals at each SCF iteration according to a criterion of maximum overlap with the starting guess for that iteration.[4] However with an overlap criterion for selecting occupied orbitals, there is a danger of converging to an excited state, especially if the changes from the initial trial guess are large. When this occurs, it is necessary to change the order of the occupied and virtual orbitals, perhaps in several steps, until one converges to the lowest energy state for the core-hole configuration. This is an arduous manual procedure. We have implemented a procedure to avoid this manual effort and to insure automatic convergence to the desired state.[28] In the spirit of Jolly's equivalent core approximation,[29,30] we replace the C atom to be core ionized with a N atom and determine the HF ground state orbitals for the closed shell positive ions for this equivalent core molecule where it is not necessary to use the overlap criterion to select the occupied orbitals. For the calculations on this equivalent core molecule, we use the same basis set as for the real molecule of interest so that the orbitals for the fictitious molecule can be used as the initial trial functions for the calculations on the core-hole state of the real molecule. For these latter calculations, it is only necessary to specify that the 1s orbital centered on the equivalent core atom is singly occupied. Since the equivalent core orbitals are a good approximation to the orbitals of the lowest core-hole state,[4] there is no difficulty in converging to the desired state without manual intervention except for the preparation of the input files.

The XPS intensities for these main peaks were determined on the basis of the Sudden Approximation, SA.[4,17] In the SA, the electronic wavefunction at the instant of photoionization, time t = 0, is taken as the wavefunction where an electron is removed from an occupied C(1s) orbital but all orbitals are fixed, frozen, as they were variationally determined for the ground state. In other words, no relaxation is allowed at the instant of photoionization. However, this wavefunction is not an eigenfunction of the Hamiltonian and the intensity that is obtained for one of the fully relaxed and screened core-hole wavefunctions is determined, within the SA, by taking the overlap of the t = 0 wavefunctions with the various ΔSCF wavefunctions where the removed C(1s) electrons have been fully screened.[4] Since the orbitals of the set optimized for the hole-states are not orthogonal to the orbitals of the set optimized for the ground state, GS, it is necessary to use a sum over overlap integrals times a minor of the overlap determinant between the GS and the core-hole orbitals.[31] A cofactor method was used to determine these many electron overlap integrals.[32] All calculations of the XPS hole-states and SA intensities were performed using the CLIPS program system.[33]

III. EXPERIMENTAL DETAILS

Poly-epoxy samples are synthesized in an Ar glovebox from the stoichiometric mixture of 2 moles of DGEBA and 1 mole of EDA. After 7 min of stirring, a thin droplet is deposited on a 10×10 mm^2 Si coupon. The first step of polymerization is performed at ambient temperature, for 48 h. Post-curing is also performed in the glovebox at 140 °C for 2 h. With this protocol, IR spectroscopy analysis shows a polymerization rate of more than 93 ± 3%, consistently. Samples are then stored in a load-lock transfer chamber at 5×10^{-8} mbar in order to outgas overnight at room temperature. Then, they are transferred directly to the XPS chamber for analysis of the as-synthesized poly-epoxy surface, including a short exposure to air.

X-ray photoelectron spectroscopy is performed with a K-alpha apparatus (Thermo Scientific) equipped with a monochromatic Al Kα source (hν = 1486.6 eV), at a pass energy of 30 eV which results in a FWHM of 0.7 eV on the Ag3d$_{5/2}$ peak of a silver standard. The FWHM of the Ag peak is commonly taken as providing an estimate of the experimental resolution of the XPS spectra. There is also a Franck-Condon, FC, broadening related to changes in the equilibrium geometry for the core-hole state that leads to an additional broadening due to excitations to vibrationally excited states for the core-hole final state; see Ref. 34. The vibrational spacing of C(1s) hole states of CO has been measured to be 0.3 eV,[35] and it is reasonable to take the Gaussian broadening for the C(1s) hole state as being the experimental resolution plus a conservative estimate of the FC vibrational broadening of 0.2 eV for a total of 0.9 eV.

IV. RESULTS

The left frame of Table I shows results obtained from ΔSCF calculations. C1s orbitals can be identified from the atom numbering of the first column derived from the model dimer shown in Fig. 1. Chemical shifts (ΔBEs)

TABLE I. Left: Calculated chemical shift (ΔBE) and intensities for each orbitals of the dimer molecule shown in Fig. 1. Center: Functional group identification (the orbital of interest belong to atoms marked with an asterisk). Right: The number and relative concentration of C1s orbitals in the solid poly-epoxy from the stoichiometric ratio 2DGEBA:1EDA. Italic rows correspond to the orbitals which are present in the model dimer, but no longer present in the fully polymerized solid.

Model dimer				Poly-epoxy (2 DGEBA + 1 EDA)	
Orbitals ID	ΔBE(ΔSCF) (eV)	Calculated relative intensity	Functional groups	Number of C1s orbitals	Relative composition
C6	0.00	0.68	C_{ph}^{*}–C_{quater}	2	9.1%
C25	0.03	0.68	C_{ph}^{*}–C_{quater}	2	
C2	0.04	0.67	C_{ph}	2	
C29	0.08	0.68	C_{ph}	2	
C5	0.14	0.67	C_{ph}	2	
C30	0.16	0.67	C_{ph}	2	36.4%
C4	0.22	0.68	C_{ph}	2	
C26	0.24	0.67	C_{ph}	2	
C3	0.25	0.68	C_{ph}	2	
C27	0.25	0.68	C_{ph}	2	
C50	0.26	0.74	CH_3	2	9.1%
C46	0.28	0.74	CH_3	2	
C24	0.82	0.74	C_{quater}	2	4.5%
C18	1.00	0.75	N–C–C*–N	2*	4.5%
_C20_	_1.20_	_0.75_	_N(H_2)–C*–C–N_	_0_	_n/a_
C16	1.25	0.75	N–C*–C(OH)	4	9.1%
C1	1.89	0.65	C_{ph}^{*}–O–C	2	9.1%
C28	1.92	0.65	C_{ph}^{*}–O–C	2	
C9	2.09	0.74	C–OH	4	9.1%
C8	2.36	0.73	C*–O–C_{ph}	4	9.1%
_C34_	_2.58_	_0.73_	_Epoxy_	_0_	_n/a_
_C33_	_2.59_	_0.73_	_Epoxy_	_0_	_n/a_
_C32_	_2.65_	_0.74_	_Epoxy-C*–O–C_{ph}_	_0_	_n/a_

are all obtained from the orbital with the lowest energy (C6), fixed at 0 eV. The third column shows the theoretical intensities calculated in the framework of the SA. The relative SA intensities range between 0.65 and 0.75 meaning that depending on the C atom, 25%–35% of the XPS intensity is lost from the main peak to shake satellites. These data are used to build the theoretical C1s spectrum by computing a Voigt convolution for each individual contribution. The Voigt convolution consists in the convolution of a Gaussian and a Lorentzian function,[36] with FWHM of 0.9 eV and 0.1 eV,[37] respectively. The spectrum envelope is the sum of all contributions.

Fig. 2(a) shows an experimental result with an empirical peak decomposition based on literature data, experience, and knowledge about the polymer composition. After the fitting procedure, a fair assessment of the poly-epoxy surface is possible with 3 contributions plus the shake-up satellite, only. These 3 contributions correspond to C–C/C–H, C–N, and oxygenated bonds. Whereas it is correct in terms of composition (in conjunction with O1s and N1s decomposition, not shown) and chemical shifts, the accuracy is limited for the description of the surface chemistry, i.e., peaks are broad (e.g., 1.6 eV FWHM for the C–O–C, C–OH peak) and hide finer details. ΔBE(ΔSCF) and SA results are presented in Fig. 2(b) with the comparison of the experimental (blue dotted line) and simulated (black full line) spectra. It helps distinguishing 9 contributions instead of 3 as the "empirical case"; hence it provides more information than is obtained from the imperfect resolution of the XPS experimental data.

In Fig. 2(b), a Tougaard background[38] is subtracted from the experimental spectrum and the simulated spectrum is positioned by applying a rigid shift until the maximum intensity matches the maximum experimental intensity (normalized to 1.0). The agreement between the experiment and the theory is rather good. The most serious limitation is that the theoretical energy of the second peak at approx. 2.3 eV is too high with respect to experiment by 0.3 eV. The intensity of this peak is also too low by 25%. Finally, there is a difference at the leading, low BE edge of the spectra.

The identification of the bond responsible for the chemical shift of the atomic orbitals BEs is shown in the central column of Table I. Some mixing was present for the C(1s) orbitals in the initial, GS, state calculations where some of these orbitals were not localized exclusively on a single C atom but were distributed over a few of the C atoms; this occurred especially when the C(1s) orbital energies were nearly degenerate. However, the singly occupied C(1s) orbitals of the ionic state HF wavefunctions were all localized on a single C atom. The fact that the initial state C(1s) orbitals were sometimes not localized was taken into account in our calculation of the SA relative XPS intensities. Nine different environments can be identified from the data in Table I and the model molecule in

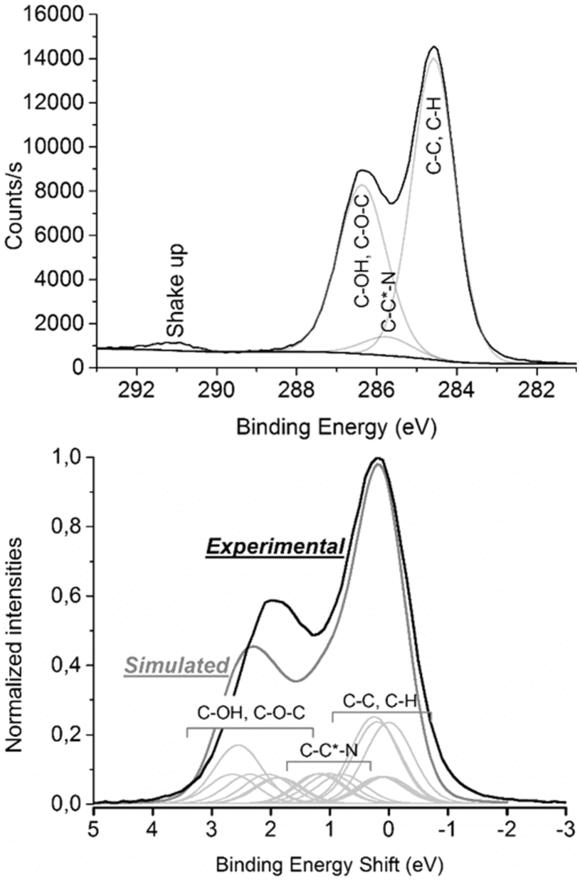

FIG. 2. (a) Experimental C1s spectrum decomposed empirically. (b) Comparison of the experimental and simulated C1s spectra obtained from the sum of the calculated contributions of each orbitals.

Fig. 1 (the relevant C atom orbital is marked with an asterisk), with the following method.

1. C_{ph}^{*}–C_{quater}: C6 and C25 of the phenyl ring bonded to the unique quaternary carbon, C24.
2. C_{ph}: C atoms of the 2 phenyl rings (C2-5, C26, C27, C29, and C30).
3. CH_3: C46, C50.
4. C_{quater}: quaternary C (C24).
5. N–C–C*–N: C–N bond within the EDA molecule (C18). C20 is discarded because it is bonded to a primary N(H_2) which shifted its 1s electron BE by +0.2 eV as compared to C18, whereas it is absent of the real surface. As a consequence, C18 is counted twice (C18 + "actual" C20).
6. N–C*–C(OH): C–N bond of the DGEBA molecule (C16) somehow shifted by the neighboring C–OH.
7. C_{ph}^{*}–O–C: C atoms of the phenyl rings (C1 and C28) bonded to O (O7 and O31).
8. C–OH: C9.
9. C*–O–C_{ph}: C atom from the DGEBA chain (C8). C32 is discarded because the neighboring epoxy ring shifts its 1s electron BE by 0.29 eV as compared to C8, whereas it is absent of the actual surface.

Therefore a first consequence of using theoretical modeling is that it offers the possibility to decompose the XPS spectra with many contributions that are guaranteed by the theory. In that sense, the 3 broad contributions of Fig. 2(a) now decompose into

- C–C, C–H → phenyls C (ΔBE = +0 to 0.25 eV) + CH_3 (ΔBE = +0.26 to 0.28 eV);
- C–C*–N → C–C*–N within EDA (ΔBE = +1.00 eV), C–C*–N within DGEBA (ΔBE = +1.25 eV), and an additional non-negligible quaternary C atom contribution (ΔBE = +0.82 eV); and
- C–O–C, C–OH → C–O–C (ΔBE = +1.89 to 2.36 eV), C–OH (ΔBE = +2.09 eV).

Therefore, to finely decompose the XPS experimental details of the C1s peaks of a polymer composed of similar bonds, acquired in similar conditions (e.g., pass energy and apparatus resolution), it may be appropriate to use a small FWHM broadening for localized contributions (such as CH_3, C–C*–N, quaternary C, and C–OH), and a larger broadening when an *apparently similar environment* allows a modest variation of the BE shifts from these C atoms as, for example, for the phenyls and the C–O–C, in the present work. We describe such variation of the ΔBE as a Δ(ΔBE).

Overall, from the interpretation of both spectra in Figs. 2(a) and 2(b), we state that the assignment of each bond at specific ΔBE is correct and can be used to describe the poly-epoxy surface. Limitations and perspectives are discussed in Sec. V.

V. DISCUSSION

In Fig. 2(b), we observe discrepancies between experiment and theory in terms of position of the higher-BE peak, relative intensities, and at the low-BE edge of the spectra.

Improvement to the HF calculations could include using larger basis sets than the DZ + basis sets we have used which may be responsible for the positioning of the second peak at a too high BE. In particular, we could consider increasing the size of the s basis set and adding a d polarization function for the C, N, and O atoms, i.e., a (5,4,1) contracted basis set for these atoms and, possibly, a (3,1) contracted basis set for the H atoms. The larger basis sets for C, N, and O atoms might allow better screening of the core-holes that could shift the energies and intensities of the different C(1s) peaks and correct the actual difference. Another possible limitation is that HF calculations do not include static electron correlation effects; such static correlation effects, especially those involving promotion from occupied bonding pi orbitals to unoccupied anti-bonding pi orbitals could change energies and intensities. In the study of the much simpler CO,[39] the static correlation from promoting 1pi(2) to 2pi(2) appears to have a significant effect on the 1s BEs. However, treating this static correlation would be much more complex in the large systems presented here than for the much simpler case of CO. Another improvement of the fit could be the use of a different Voigt function with a larger Gaussian width. But, we are reluctant to use the Gaussian broadening as a free parameter since it would introduce an empirical character into the study.

Anyway, before any of the theoretical parameter is modified, there is another limitation that surpasses all the

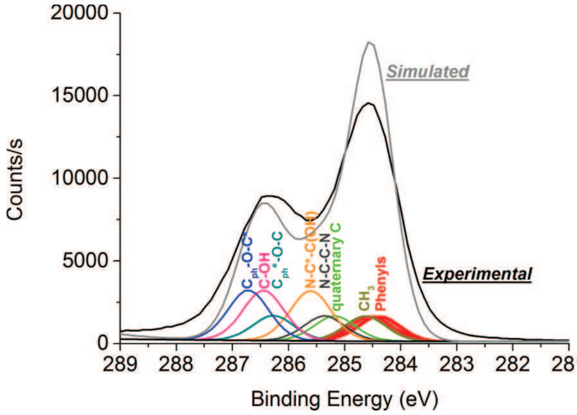

FIG. 3. C1s spectra decomposed using the ΔBE(ΔSCF) results along with the actual stoichiometry.

others which is the size of the dimer model; although it allows a correct description of the chemistry of the system, it is not correct for the estimation of intensities because it does not respect the actual stoichiometry. Supporting evidence for this assertion is shown in Fig. 3 where the C1s peak decomposition is obtained by using ΔBE (ΔSCF) corrected from the stoichiometric composition obtained by dividing the number of orbitals in a particular family (see Table I, LEFT) over the total number of C1s orbitals, 44, in the bulk solid.

We observe a better positioning of the second peak at about 286.5 eV. Nevertheless, discrepancies remain in the BE region between 285.5 and 286 eV, and at the leading low-BE edge of the spectra. Additionally, the total intensity of the phenyls and CH_3 contributions is higher than experiment by about 20%. Nevertheless, intensities corrected from stoichiometry indicate that the poly-epoxy surface is close to a bulk truncation. The surface may be enriched in oxygenated species since the second higher-BE peak relative intensity is higher in experiment than in theory.

The only way to further improve our results would be to start from a different model that could take into account the neighboring chains and the presence of vacuum, i.e., moving towards a semi-infinite model mimicking a *surface* instead of a *molecular* model. This is a long-term objective since it involves creating such a surface by cutting a small cluster into a large model surface obtained, for instance, by classical molecular dynamics and Monte Carlo calculations. With this strategy, a large system is allowed to relax in the presence of vacuum at a given temperature, and a slab can be extracted for electronic structure calculations with a limited number of atoms.

VI. CONCLUSIONS

We have presented a detailed description of the C1s spectrum of a poly-epoxy surface with the aid of theoretical calculations of the relative binding energies and intensities of the peak components. Whereas HF calculations have proven their robustness in the framework of the ΔSCF methodology for small molecules,[4,12–14] we have extended these applications to a molecule of poly-epoxy, which contains 61 distinct and symmetry inequivalent atoms, with a fairly good success. A decomposition of the C1s peak by an experienced experimentalist yields to only three environments for the C atoms, i.e., C–C/C–H, C–N, and C–OH/C–O–C, plus the shake satellite. Supported by HF calculations, one now decomposes the same peak into 9 contributions with well-defined origins, some of them being traditionally lost in a larger global contribution (e.g., the quaternary C atom where we usually attribute C–N contributions). In addition, we notice that whereas some contributions are found at specific ΔBE with regards to the reference peak, and others allow more or less large Δ(ΔBE). For instance, in the present study, C–O–C environments spread from ΔBE = +1.89 eV to ΔBE = +2.36 eV because of the variation of the polarization of neighboring bonds. In this specific case, one should add Δ(ΔBE) = 0.47 eV to the FWHM of the contribution in order to account for the uncertainty about its relative position. This additional broadening is naturally taken into account in the analysis of the ΔSCF wavefunctions; nevertheless, with the theoretical guidance that we have provided, it could also be included in the empirical analysis and assignments of the experimental XPS data.

In order to improve the matching between experimental and simulated spectra, we have proposed several directions including the increase of the size of the basis sets used in the HF calculations and the involvement of electronic correlation effects. However, perhaps the most immediate and pressing need is to develop an improved model for the surface of the polymer.

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