



Ab initio calculations for XPS chemical shifts of poly(vinyl-trifluoroacetate) using trimer models

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ABSTRACT

X-ray photoelectron spectra (XPS) of the polymer poly(vinyl-trifluoroacetate) show C(1s) binding energy shifts which are unusual because they are influenced by atoms which are several bonds away from the probed atom. In this work, the influence of the trifluoroacetate substituent on the 1s ionization potential of the carbon atoms of the polyethylene chain is investigated theoretically using mono-substituted, diad and triad models of trimers representing the polymer. Carbon 1s ionization energies are calculated by the Hartree–Fock theory employing Koopmans' theorem. The influence of the configuration and conformation of the functional groups as well as the degree of substitution are found to be important determinants of XPS spectra. It is further found that the 1s binding energy correlates in a linear fashion, with the total electrostatic potential at the position of the probe atom, and depends not only on nearest neighbor effects. This may have implications for the interpretation of high-resolution XP spectra.

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1. Introduction

X-ray photo electron spectroscopy (XPS) is an important tool for chemical analysis of materials, including complex polymeric surfaces. The XPS analysis of insulating samples requires a neutralization of the positive charges left by the leaving photoelectrons. In order to make sure that the neutralization is complete and no residual charge can cause a deformation of the spectrum, the charging is usually over-compensated. This results in a slightly varying binding energy scale for every sample. If organic materials are investigated, the aliphatic carbon atom is often used as a reference with a binding energy (BE) set to 285.0 eV [1]. This approach is reasonable and avoids using an external reference such as an evaporated gold coating on the sample [2]. However, this simple procedure sacrifices the possibility to compare different samples unambiguously.

In general, the chemical shift is influenced by the electrostatic potential at the particular atom which is ionized. In a simple idealization, the potential is caused by the partial charges in the molecule due to polar bonds [3]. For XPS data interpretation usually only the neighboring atoms are taken into consideration. For example, an oxygen atom bound to a carbon atom shifts the C(1s) binding energy by about 1.5 eV to higher values, and two oxygen atoms cause

a shift of about 3.0 eV [1]. Small variations due to the second neighbor have been reported for the carbon atoms next to a carboxylic group (three bonds to oxygen) [3] and the carbon next to a carbon atom with bonds to fluorine [4,5]. The shifts are about 0.4 eV in the first case and 0.7 eV in the latter, respectively.

The chemical derivatization of surface functional groups can be used to determine the concentration of these groups. For the derivatization of hydroxyl groups trifluoroacetic anhydride (TFAA) is used. TFAA also tags amines. Recently, results of derivatization experiments with TFAA were reported which revealed that the binding energy of the CF₃ carbon atom varies depending on whether it is bound in a trifluoroacetate (second neighbor O), or in a trifluoroacetamide (second neighbor N) [6,7]. Moreover, it also varies with the density of the functionalizing groups. In poly(vinyl-trifluoroacetate) (PVTFA), which carries a trifluoroacetate group on every second main chain carbon atom the CF₃ BE was determined as 294.4 eV. The BE of the same atom in an isolated trifluoroacetate group in trifluoroacetic acid modified poly(vinyl-butylal) (PVB) was found to be 293.6 eV, and 292.2 eV in a trifluoroacetamide (poly(vinyl-amine), PVAm). The comparison of these samples was made possible by using polyethylene (PE) as the same external charging reference. Since all of these examples show the reaction products of trifluoro acetic anhydride with hydroxyl groups or amines, the derivatization can provide information about the concentration of these groups and in addition about their chemical environment.

These experiments also revealed that in the case of PVTFA, the unsubstituted main chain carbon can be shifted by 1.6 eV compared to the carbon atoms in polyethylene. Note that the highly electronegative substituents (fluorine) are five bonds away [7] in this case. It is,

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at first glance, hard to imagine how these long-range effects can have an influence on C(1s) XP spectra, which are thought to be dominated by nearest and next nearest neighbor interactions. In order to quantify and understand this long-range effect, we performed *ab initio* calculations on trimer models of PVTFA.

Various methods to calculate core–electron binding energies are established in the literature. An estimation of BEs can be obtained by Koopmans' theorem [8], i.e., $BE = -\epsilon_i$, where ϵ_i is the Hartree–Fock energy of orbital i of the neutral species, which is to be ionized. Since only the neutral species is considered, this approach neglects relaxation effects. The latter are, however, partially compensated for by the simultaneous neglect of electron correlation in Hartree–Fock. To account for orbital relaxation, BEs can be calculated as energy differences between core-ionized cation and neutral molecule, $BE = E(A^+) - E(A)$. This approach is known as Δ SCF (self-consistent field), Δ MP2 (Møller–Plesset 2nd order) or Δ CI (configuration interaction), depending on the method used to calculate the electronic structure. Δ SCF, which lacks electron correlation in contrast to the other mentioned methods, usually underestimates the electron binding energy by several hundred meV as shown by Deutsch and Curtiss on small molecules using various basis sets [9]. Density functional theory (DFT) is also used to determine core binding energies. Based on the ideas of Slater's transition state (TS) theory [10], which was later generalized (GTS) by Williams et al. [11], Chong proposed the so called unrestricted generalized transition-state (uGTS) method [12,13] and tested it for over 50 molecules, showing that the average absolute deviation of the calculated values from the experimental ones is in the order of 0.2 eV [14]. In Slater's TS theory the (core) electron BE is obtained by performing only a single self-consistent field calculation at an intermediate state half way between initial (neutral) and final (ionized) state with an occupation number of one half for the respective orbital [10]. As shown by Williams et al., the error with respect to the exact energy difference can be reduced by one order in the series expansion if the initial state and an intermediate state that is not the midpoint to the final state, i.e. with a fractional orbital occupation number different from one half, are used [11]. An even smaller deviation from experimental data, in the order of 0.1 eV, was found by Kuramoto et al. employing the SAC-CI (symmetry adapted cluster configuration interaction) method [15,16] for molecular core ionization spectra with satellite structures [17]. Core electron BEs of several polymers using dimer models were calculated by Otsuka et al. employing uGTS [18,19].

For XP spectra of polymers one has the principle choice of using periodic [20] or finite oligomer models [21]. The former have the advantage of accounting for band structure effects, however, they can be costly in particular if systematic studies of composition, configurations, and conformations are to be considered. Since this is the major concern of this paper, we will use oligomer models in the following. In particular, trimer models will be used which allow for a systematic variation of substitution and geometry parameters. Also, dimer models and periodic models have been used for testing, which will not be mentioned further in this paper, however, because they appeared to be less flexible in particular if large unit cells are to be avoided. Further, Hartree–Fock-based Koopmans' theorem will be used to be able to consider a large number of models. In this context it is worthwhile to note that employing Koopmans' theorem, Duke and O'Leary found a better agreement with experiment for XPS shifts of fluorinated PE when using finite model compounds in contrast to models based on periodic boundary conditions [22].

The manuscript is structured as follows. In Section 2 experimental details and results adopted from Ref. [7] are reviewed. The following Section 3 briefly introduces the applied theoretical methods and explains the molecular model used for the calculations. The results of the simulations are presented and discussed in Section 4. Section 5 summarizes the results.

2. Experiment

Poly(vinyl-trifluoroacetate) (PVTFA) was prepared by esterification of poly(vinyl-alcohol) (PVA) with trifluoroacetic anhydride (TFAA), using one of the two following reaction techniques [7]:

- A PVA is coated on PE and transferred to a steel chamber which is evacuated afterwards. Then TFAA is evaporated into the chamber.
- B PVA is soluted in water and TFAA is slowly added. Afterwards the product is cleaned and dried.

For reaction condition A a yield of 97% was reached. Reaction B yielded merely 14% product. The reasons for the different yields were detailed in Ref. [7]. Here it is sufficient to note that the yield Y was determined by [7]

$$Y = \frac{[X]^{exp}}{[X]^{stoich}} \cdot 100\%, \quad (1)$$

where $[X]^{exp}$ is the experimentally determined concentration of the functional group, and $[X]^{stoich}$ is the theoretical concentration of the completely transformed molecule. Therefore, the higher Y , the higher is the density of trifluoroacetate (TFAC) groups along the polymer chain. A yield of 100% would correspond to $[\text{CH}(\text{TFAC})-\text{CH}_2]_n$. XP spectra were recorded of the products. The observed C(1s) energies and the respective chemical shifts are listed in Table 1, with Fig. 1(a) showing the monomer with the numbering of atoms. Exemplarily, the XP spectrum of PVTFA for reaction condition A with 97% yield is given in Fig. 1(b), in comparison to that of PE.

From Table 1 we note that the high-concentration (A) case differs substantially from the low-concentration (B) case as far as C(1s) shifts relative to PE are concerned, with the following trends: for high TFAC concentrations (A), chemical shifts relative to PE are larger than for low TFAC concentrations (B); further, the shift increases considerably in the order $C_1 < C_2 < C_3 < C_4$. Note in particular that the TFAC group has an influence on the shift of C_1 , despite the F atoms are, formally, separated by five bonds from C_1 as mentioned earlier. It is our goal to explain these effects by quantum chemical calculations.

3. Theory

3.1. Model and method

The shift of the 1s binding energy for carbon atom k , ΔE_k , is defined as the difference of the 1s BE of a reference carbon, $E_{1s}(C_{ref})$, and the 1s BE of carbon k :

$$\Delta E_k = E_{1s}(C_{ref}) - E_{1s}(C_k). \quad (2)$$

The reference energy, $E_{1s}(C_{ref})$, is the 1s ionization energy of the carbon in PE in the experiment [7]. For the simulations, the 1s electron binding energy of the C atom of heptane which corresponds to C_1 in Fig. 1(a) is used as reference (see below).

Specifically, PVTFA is modeled by a trimer model assuming the typical head–tail configuration and a zigzag conformation of the

Table 1
Binding energies of carbon 1s electrons in eV for reaction conditions A and B. The chemical shifts refer to the C(1s) energy of polyethylene, PE (285 eV). The numbering of the atoms is given in Fig. 1(a). The reaction yield is given in percent. All values are adopted from Ref. [7].

Reaction (yield)	C_1	C_2	C_3	C_4
A (97%)	286.6	288.4	291.2	294.3
B (14%)	285.0	287.5	290.2	293.3
Shift A	1.6	3.4	6.2	9.3
Shift B	0.0	2.5	5.2	8.3

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