Accurate Density Functional Calculation of Core XPS Spectra : Towards an Evidencing of Intermolecular Effects at Real Interfaces via XPS ?

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Core levels X-ray Photoelectron Spectroscopy (XPS) is routinely used to obtain information on the chemical composition, bonding and homogeneity of molecules, surfaces or interfaces. In spite of their apparent conceptual simplicity, Core-Electron Binding Energies (CEBEs) a few electron-volts (eV) or fraction of an eV apart are difficult to interpret. Moreover, the attribution of chemical structures and/or geometries cannot always be done in analogy with gas-phase molecular structures or stoechiometries when unknown compounds are formed. Toward this aim, quantum-chemistry based computations have proven an invaluable help in the understanding of XPS spectra. The most powerful theoretical methods so far used in this field involve *ab initio* post-Hartree-Fock finite difference calculations, such as CASSCF, CI or MP2, and deliver predicted CEBEs with an average absolute deviation (aad) of the order of 0.5 to 1.0 eV. In the present paper, we describe recent procedures of computing accurate Core-Electron Binding Energies (CEBEs) via Density Functional Theory (DFT). The procedures have been tested on numerous small (3-6 atoms) to fairly large (15-25 atoms) systems, and afford computed CEBEs in excellent agreement with experiment, with an aad of 0.20 eV for gas-phase systems, and about 0.30 eV for molecules chemisorbed on metallic surfaces. These absolute deviations are compatible with the best XPS experiments carried out at the moment. We suggest - on the instance of γ-APS (an adhesion promoter) and CO chemisorbed on various Pd faces - that the accurate calculation of CEBEs has now come to be a tractable and reliable alternative as a hand for spectrum decomposition on real, complex, systems when gas-phase reference XPS spectra are not available for calibration.

§1. Introduction

1.1 Computing core-electron binding energies : a historical overview.

X-ray Photoelectron Spectroscopy is among the very powerful techniques to gain informations on the chemical composition and bonding for molecules, surfaces and interfaces.1) Core-Electron Binding Energies (CEBEs) constitute the key spectral information obtained by this technique, as they are related to the physico-chemical environment a nucleus feels in a molecule.2) Early in the history of XPS (also termed Electron Spectroscopy for Chemical Analysis (ESCA) at that time), it was recognized that the CEBE of an atom should be related to the effective charge on that atom.3,4) This effective charge could in turn be correlated with intuitive concepts such as the difference between the electronegativity of bonded atoms.5) From these empirical correlations emerged a rule-of-thumb saying that the CEBE of an atom is raised when it is in a more electronegative surrounding, and that it is lowered when experiencing the effects of a more electropositive environment.1) Despite the invaluable practical usefulness of this simple rule, it is sometimes difficult to relate precisely the various CEBEs with the underlying molecular structures, especially when the CEBEs differ by a few electron-volts (eV) or fraction of an eV, as the typical resolution of XPS experiments is of the order of 0.2 to 0.5 eV, although it may be as low as 0.05 eV when the irradiation is performed with a synchrotron radiation. In these cases, theoretical calculations have proven quite useful or even indispensable to a correct interpretation.6–8)

At the simplest level, Koopmans' theorem9) provides with a straightforward method to make a rough evaluation of the CEBEs, by equating these with $-\varepsilon_k$, the opposite of the orbital energy resulting from a Hartree-Fock calculation on the neutral parent molecule. This method gives rather poor estimates of the CEBEs,10) with shifts as large as 10 to 20 eV from experimental values. This large shift is mainly due to the significant relaxation effects, which are not taken into account since the calculation is done on the neutral parent only, and which are only partly compensated by the simultaneous neglect of correlation effects.6)

At the other edge in the hierarchy of techniques used to compute CEBEs, one finds the various "ΔSCF" approaches. These consist in making the explicit computation of the electronic structure of both the neutral parent and the core-ionized species, and then calculating the energy difference between the two. The quality of the result then depends on the theoretical treatment used in the two SCF calculations. This approch takes relaxation effects into account, and the quality of the SCF wavefunction is higher when correlation effects are taken into

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account. Pretty good results have been obtained with this approach,[8)] mainly at the ΔMP2 and ΔCI levels, but the calculated CEBEs are still 0.5 to 1.0 eV apart from experimental values. This is about five times as large as the resolution of the best XPS experiments carried out at the moment. For most compounds however, the order of the core-levels is correct, and XPS spectra decompositions can be correctly interpreted in terms of molecular structures,[8,11)] which is a definite advantage over Koopmans' predictions.

In between Koopmans' and ΔSCF calculations, a method was developped termed the transition operator method,[12)] in which the Fock operator involved in the calculation of the electronic structure of the ionized species is modified so as to adjust an occupation of 1/2 in the ionized core level. Fairly good results were obtained with this approach, as well as with improved versions involving third-order perturbation corrections to the transition operator method, followed by extrapolation using a geometric approximation.[13)]

1.2 The unrestricted Generalized Transition State approach (uGTS)

The computations, however, were quite expensive, and a need for a cost-effective method enabling the accurate calculation of CEBEs was still present. Recently, Chong has proposed a method called uGTS using Density Functional (DFT) calculations,[14)] based on the ideas of Slater's transition-state (TS)[15)] later generalized by Williams et al.[16)] This method has now been tested on about a hundred of molecules, and has been shown to deliver predicted CEBEs in excellent agreement with experiment, with an average absolute deviation (aad) of only 0.20 eV from experimental results.[11,17)]

Over twenty years ago, Slater introduced the transition-state (TS) method.[15)] Consider an electronic process such as ionization or excitation at fixed molecular geometry. Let us define :

$$\begin{aligned} E(\lambda) &= \sum_k \lambda^k E_k \\ &= E_0 + \lambda E_1 + \lambda^2 E_2 + \lambda^3 E_3 + \lambda^4 E_4 + \lambda^5 E_5 + \ldots \end{aligned} \tag{1.1}$$

where $E(0)$ and $E(1)$ correspond to the initial and final states respectively and λ is assumed to be a continuous variable. The coefficients are simply related to the derivatives at $\lambda = 0$:

$$\left(\frac{\partial^k E}{\partial \lambda^k}\right)_{\lambda=0} = (k!)\, E_k \tag{1.2}$$

From equation (1.1), the difference ΔE in energy between the neutral parent molecule and the ionized species is equal to :

$$\Delta E = E(1) - E(0) = E_1 + E_2 + E_3 + E_4 + E_5 + \ldots \tag{1.3}$$

Now if we define the first derivative :

$$\begin{aligned} \Delta E &= E(1) - E(0) \\ &= E_1 + E_2 + E_3 + E_4 + E_5 + \ldots \end{aligned} \tag{1.4}$$

then, in Slater's original transition-state concept, ΔE is approximated by :

$$\begin{aligned} F(\lambda) &= \frac{\partial E}{\partial \lambda} \\ &= E_1 + 2\lambda E_2 + 3\lambda^2 E_3 + 4\lambda^3 E_4 + 5\lambda^4 E_5 + \ldots \end{aligned} \tag{1.5}$$

with an error of :

$$\delta_{TS} = -\frac{1}{4}E_3 - \frac{1}{2}E_4 - \frac{11}{16}E_5 + \ldots \tag{1.6}$$

The quantities $F(\lambda)$ can be obtained straightforwardly if the calculations are carried out within the Density Functional Theory (DFT) formalism. Indeed, for ionization of an electron from molecular orbital (MO) ϕ_k, for example, we can apply Janak's theorem[18)] and equate $F\left(\frac{1}{2}\right)$ with $(-\varepsilon_k)$, where ε_k is the MO energy resulting from a Kohn-Sham type calculation in DFT, with an occupation $1 - \lambda = \frac{1}{2}$ in level number k. In the Generalized Transition State (GTS) method, Williams et al.[16)] proposed the use of :

$$F\left(\frac{2}{3}\right) = E_1 + \frac{4}{3}E_2 + \frac{4}{3}E_3 + \frac{32}{27}E_4 + \frac{80}{81}E_5 + \ldots \tag{1.7}$$

Therefore, ΔE can be approximated by :

$$\begin{aligned} \Delta E &= \frac{1}{4}\left[F(0) + 3F\left(\frac{2}{3}\right)\right] \\ &= E_1 + E_2 + E_3 + \frac{8}{9}E_4 + \frac{20}{27}E_5 + \ldots \end{aligned} \tag{1.8}$$

with an error of only :

$$\delta_{GTS} = -\frac{1}{9}E_4 - \frac{7}{27}E_5 + \ldots \tag{1.9}$$

which is expected to be smaller than δ_{TS}. Several attempts showed that the best way to carry out the calculation with $\lambda = \frac{2}{3}$ was to perform an unrestricted computation, i.e. removing $\frac{2}{3}$ electron in the kth orbital of the α spin manifold while leaving an occupation of 1 in the kth orbital of the β spin manifold.[14)] As for the TS approach, $F(0)$ and $F\left(\frac{2}{3}\right)$ are obtained *via* the MO energies of the partially emptied Kohn-Sham orbitals. Hence, at least (M+1) SCF calculations have to be carried out to obtain M CEBEs : the one on the parent neutral molecule, and at least M SCF calculations with a partial core-hole localized on the M desired atomic centers.

The best results have been originally obtained[14)] with the large cc-pV5Z correlation-consistent valence quintuple zeta basis sets of Dunning et al.,[19)] but results of comparable accuracy (±0.07 eV) are now delivered with much smaller basis sets of triple zeta quality[17] in which the exponents of the cc-pVTZ set describing the core-hole are scaled according to the proposals of Clementi and Raimondi.[20] We will illustrate this point for various core levels (C1s, N1s, O1s, F1s) by presenting some results obtained on small molecules with increasing basis set quality. This reduction in the size of the basis set enables to treat larger systems with the same procedure,[11,21] and we will illustrate this on γ-Amino Propyl trihydroxy Silane molecule (γ-APS), a molecule which is used as an adhesion promoter in the coating of oxidized silicon wafers with poly-imide films.[22] Our calculations brought a decisive information enabling a safe XPS spectrum decomposition for the adsorbed compound, for which no gas phase reference spectrum can be obtained.[23]

1.3 A new procedure for chemisorbed molecules

The second method we present herein, which also makes use of DFT, has been especially adapted to obtain accurate CEBEs for molecules chemisorbed on metallic surfaces. A truly new procedure turned out to be necessary, as we also wanted to describe the metallic surface using clusters. In the case of CO atop- or bridge-adsorption on cluster-modeled Pd(100) and Pd(110) surfaces, Pedocchi et al. find that the C1s and O1s CEBEs - as obtained by a direct full-hole ΔSCF procedure - are cluster-size dependent, and remain 2.5 to 3.0 eV above the experimental values even with model clusters bearing up to 13 metal atoms.[24] Using the uGTS procedure of Chong, slightly improved results were obtained, but aad's remain larger than about 1.5 eV in the same conditions.[25] This cluster-size dependence traduces the uncapability of metal clusters to render correctly the image charge of the core-ionized species, due to its finite size. Indeed, this image charge is supposed to be accomodated for by the electron gas of the metal via the interplay of Friedel-type density pseudo-oscillations. As one truncates the surface to a cluster, one imposes boundary conditions to the oscillatory phenomenon, leading to the unwanted result that it is the size and shape of the cluster which fixes the accomodation of the image charge. The procedure we have proposed overcomes this problem by decomposing the CEBE of atomic center X in a formal two step path, through which the non-relativistic CEBE $I_{nr}(X)$ of core X is decomposed according to[25] :

$$I_{nr}(X) = \Delta E\,(X \to c.b.) + \varphi^{X}\,(c.b. \to vacuum) \quad (1.10)$$

where $\Delta E\,(X \to c.b.)$ is the amount of energy required to promote the core electron from X to the conduction band of the metal ($c.b.$), and $\varphi^{X}\,(c.b. \to vacuum)$ is the residual work to take this electron from the conduction band to the vacuum at infinity. In the limit of low adsorbate coverage, the latter quantity can be replaced by the work function Φ^{M} of the bare metal :

$$I_{nr}(X) = \Delta E\,(X \to c.b.) + \Phi^{M} \quad (1.11)$$

which need not be computed. Thus, only the core-to-conduction-band excitations are explicitly calculated via DFT. This procedure turns out to be much less cluster-size dependent, as the above excitation is carried out at constant overall number of electrons and thus never deals with charged species (for which the image charge in the metal would have to be described). In the present study, excitations have been performed by promoting one electron from the desired (C1s or O1s) core level to the conduction band within the same spin manifold. The resulting Kohn-Sham determinant is not an eigenfunction of S^2anymore, but rather a mixing of singlet and triplet states.[25] However, our purpose is not the calculations of true excitation energies, and it is of no importance that the final (excited) state be not of the same spin multiplicity as the neutral parent (which is a singlet) : this difference vanishes when CO is chemisorbed on a true metal, and is thus the residual trace of the cluster approximation. The experimental work functions are 5.65 eV for Pd(100) and 5.20 eV for Pd(110).[26]

§2. Computational details

The DFT calculations were done with the deMon code[27] on a Cray C94. The set of auxiliary basis functions is (5,4;5,4) for Si, (4,4;4,4) for C,N, O and F and (3,1;3,1) for H.[28] The orbital basis sets are Dunning's cc-pVDZ, cc-pVTZ, cc-pVQZ and cc-pV5Z on Si, C, N, O, F and H.[19] As previously,[29] scaled-pVTZ basis sets have also been used on the partially ionized atomic centers in order to better describe the core-hole. The results obtained with all these basis sets are compared. Only s-, p- and (six components) d-type functions were used. The numerical integration for the fit of the exchange and correlation potentials into the auxiliary basis set is performed using a grid having 32 radial points × 194 angular points per atom. The functionals are Becke's 1988[30] for the exchange term and Perdew's 1986[31] for the correlation term.

When performing the SCF calculation on the ionized species, one has to deal with the problem of core-hole localization.[12] This problem arises during the SCF iterations when two (or more) core levels are close in energy eventhough they correspond to atomic centers which are spatially separated (by whatever distance), as the core-hole may spatially jump from one center to the other during successive iterations. This behavior precludes any convergence of the SCF procedure. Various strategies have been designed to come around this problem, and consist in performing preliminary calculations on iso-electronic species with fictitious nuclear charges on the center at which one wishes to localize the partial core-hole, in order to "prepare" the correct electronic density around it. This can be done first by forcing the core-hole (which is positive) on the desired atom by lowering its nuclear charge (B^- replacing C...etc). In that case, the core region is better prepared than the valence region. Alternatively, one can provide a good guess for the valence region around the core-hole by raising the nuclear charge of the desired atom (N^+ replacing C...etc), hence making the so-called "equivalent-core" approximation.[6,12] Both techniques were used in our various calculations, and lead to guess densities of comparable quality as regards the remaining number of iterations to carry out in order to reach full convergence with the correct skeleton. The use of these techniques enables one to reach correct convergence for atoms with calculated CEBEs separated by no more than 0.1 eV, which is quite promising for the study of large molecules, and polymers in particular.

In order to compare the calculated CEBEs with experiment, we need an evaluation of relativistic effects (which we do not take into account explicitly in the quantum mechanical treatment). A crude estimate of relativistic corrections can be made by adding to the theoretical values the quantity[29) :

$$C_{rel} = K.I_{nr}^{N} \qquad (2.1)$$

where $K=2.198.10^{-7}$ and N=2.178, when both I_{nr} and C_{rel} are in eV. In what follows, all CEBE values are referenced to the vacuum level, unless otherwise mentioned.

In the study of γ-APS, two distinct types of geometry optimizations were performed. The geometry of each and every isolated molecule (γ-APS, methylammonium, the hydrogen carbonate ion and water) was carried out at the MP2/6-31G** level using the GAMESS code[32) on a 128-node Cray T3D. Interaction geometries between the above molecules are considered on the basis of Van der Waals interactions only, according to the simulated annealing procedure of Claverie.[33,34)

§3. Calculation of CEBEs

3.1 Test molecules. Basis set effects.

In Fig.1, we present a comparison of experimental vs computed C1s CEBEs for ten small molecules (ranging from CH_4 to CH_3COOH), obtained with basis sets of increasing quality, ranging from the correlation-consistent valence double-zeta cc-pVDZ to the correlation consistent valence quintuple-zeta cc-pV5Z set of Dunning et al.[19) One sees that an optimum aad of the order of 0.20 eV is obtained with cc-pVQZ, which is not improved anymore upon using the larger cc-pV5Z set. One significant improvement made by Chong has been to design scaled basis sets, in which the exponents of the gaussian primitives are scaled by a factor taking into account the partial screening of the fractional hole made in the core levels.[17) In Fig.2, the results obtained with the scaled-pVTZ basis set designed by Chong are presented, and prove to be extremely good, as they are almost identical with the ones obtained with the much larger cc-pV5Z basis set. This ascertains the use of the scaled-pVTZ as a very good basis set for our present calculations, since the cc-pV5Z set is known to approximate the basis set limit very well.[36) In Fig.3, we present a comparison between our present DFT/uGTS/B88-P86/scaled-pVTZ procedure (aad = 0.11 eV), and the best one which was previously available (ΔMP2/TZP, aad = 0.56 eV) on acetonitrile (CH_3CN), propionitrile (CH_3CH_2CN) and acrylonitrile ($H_2C{=}CHCN$) molecules, for which the XPS spectra were measured in the gas-phase with high precision. Residual deviations from experiment may originate from various sources. First an overall precision of ±0.1 eV is to be expected on the experimental values, as illustrated by the slight variations between CEBEs originating from different groups.[35) Second, the evaluation of relativistic effects (equation (2.1)) is only approximate.[37) Third, the present method is based on an approximate equation (1.8), and one would have to make an evaluation of the remaining error (equation (1.9)). Fourth, the exchange and correlation functionals of Becke and Perdew are definitely local, though gradient-corrected. In a series of molecules of very similar structures, weak but systematic discrepancies appear due to the presence of conjugating effects. We think that these may be due to truly nonlocal effects the present functional cannot completely account for. On the whole however, the aad falls as low as 0.20 eV, hence showing that the present method is very accurate for the systematic computation of CEBEs.

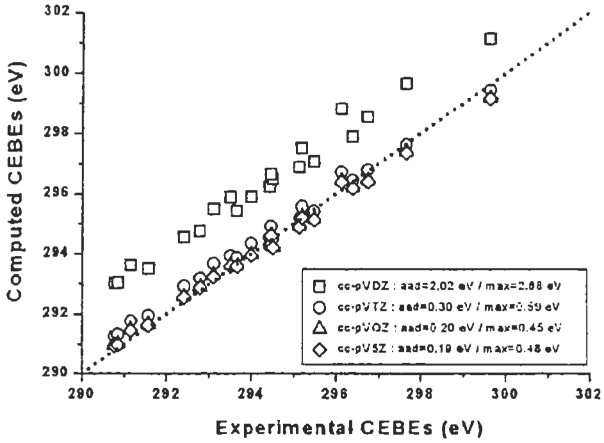

Fig. 1. Experimental vs computed (DFT/uGTS/B88-P86) Core-Electron Binding Energies (in eV) for small reference organic molecules in the gas phase. Both the average absolute deviation (aad, in eV) and the maximum deviation (max) are indicated for all cc-pVDZ (squares), cc-pVTZ (circles), cc-pVQZ (up triangles) and cc-pV5Z (diamonds) basis sets. The unit slope line is also shown for comparison.

3.2 From interpretation to simulation.

3.2.1 Evidencing intermolecular effects with XPS : γ-APS as a probe.

Poly-imides are commonly used as surface coatings on silicon wafers in micro-electronics. As they show high temperature stability, good mechanical properties, low process temperature and easy surface planarization, they are well suited for packaging applications. On the other hand, poly-imides suffer from poor adhesion characteristics. To overcome this problem, adhesion promoters such as γ-Amino Propyl triethoxy Silane (γ-APS : $H_2N\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}Si(OCH_2CH_3)_3$) are used to pre-condition the silicon substrates on which the polymer is deposited.[44) The very mechanism of the interaction of γ-APS with actual silicon wafers is difficult to elucidate due to the com-

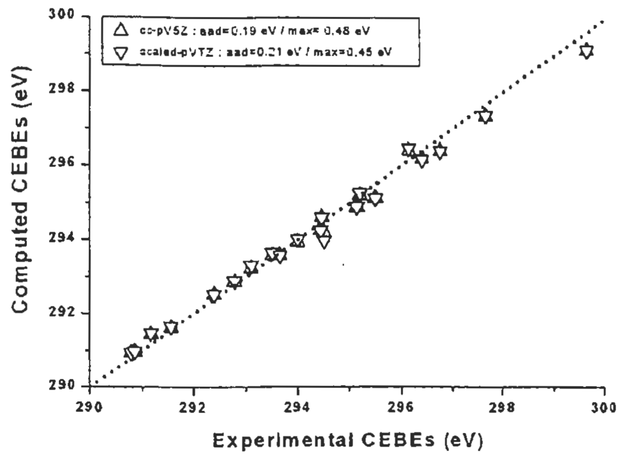

Fig. 2. Experimental vs computed (DFT/uGTS/B88-P86/scaled-pVTZ) Core-Electron Binding Energies (in eV) for small organic molecules in the gas phase. Both the average absolute deviation (aad, in eV) and the maximum deviation (max) are indicated for the cc-pV5Z (up triangles) and scaled-pVTZ (down triangles). The unit slope line is also shown for comparison.

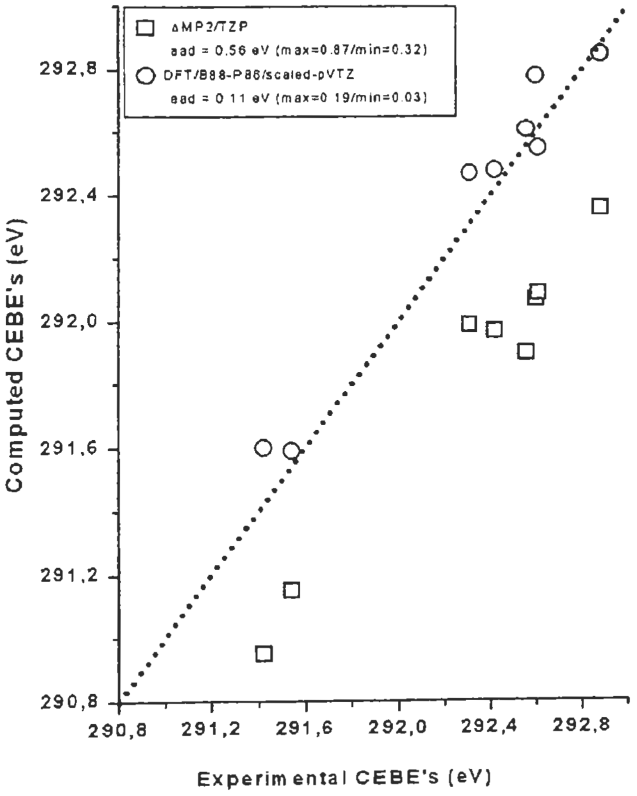

Fig. 3. Experimental vs computed Core-Electron Binding Energies (in eV) for acetonitrile, propionitrile and acrylonitrile in the gas phase. Theoretical values have been obtained at the DFT/uGTS/B88-P86/scaled-pVTZ (circles) and ΔMP2/TZP (squares) levels. Both the average absolute deviation (aad, in eV) and the maximum deviation (max) are indicated in the insert. The unit slope line is also shown for comparison.

plexity of the system, and a number of molecular models have been proposed for the molecular structures occuring at the silicon/γ-APS interface.[44] These models rely on an analysis of experimental informations obtained via Infra-Red Spectroscopy and X-ray Photoelectron Spectroscopy (XPS).

In this last field, the C1s, N1s, O1s and Si2p regions have been examined in order to detect chemical shifts upon molecule/surface interactions, but no detailed attribution of the various Core-Electron Binding Energies (CEBEs) to precise structural modifications have been proposed, to our knowledge. We see two reasons for this : (i) no gas-phase reference XPS spectrum can be obtained for γ-APS, as the compound oligomerizes upon warming; thus, γ-APS can only be observed deposited on a surface, i.e. already interacting with other molecules and/or with the surface; and (ii) the molecular interactions underwent by γ-APS can range from hydrogen bonds (-NH_2 groups) to true chemical bonds (surface and/or intermolecular Si-O-Si bridges) as well as ionic bonds (Si-O^-,^+H_3N-), which means that chemical shifts due to surface deposition or structural modifications can range from a fraction of an eV to several eV's. This raises some difficulties as to the possibility of safely separating various components in the decomposition of the XPS spectra of γ-APS and its by-products.

For instance, the three carbons of the γ-APS backbone are not resolved in the C1s region of the XPS spectrum of a 300 nm thick film of γ-APS deposited on a silicon wafer (Fig.4). However, the observed broad peak obviously stems from several contributions, as suggested by the Full Width at Half Maximum (FWHM) of 2.5 eV. An "objective" two-peaks decomposition (resulting FWHM's=1.5 eV) fits the experimental curve correctly, but cannot be easily related to the structure of the molecule (H_2N-CH_2-CH_2-CH_2-$Si(OH)_3$), which would suggest three peaks (one for each carbon, resulting FWHM's$\simeq$1.35 eV). In the latter case however, it is the structure of the molecule which is used to interpret the XPS spectrum rather than the other way round. This reduces considerably the *a priori* analytical power of the technique - and, in short, its interest - when trying to follow *in situ* the physico-chemical modifications of the original system under post-treatments such as thermal curing,[23] as we have to rule out one cause of peak broadening (structural changes vs intermolecular effects) to be able to conclude.

One alternative we have proposed is to make a computation of the CEBEs of an untouched γ-APS molecule, and examine whether obserbed chemical shifts are intrinsic to the molecular structure or do result from intermolecular interactions. The results are gathered in Table 1, and indicate that the C1s broad line can be safely decomposed on the basis of three peaks corresponding to each and every carbon center of an untouched γ-APS molecular skeleton.[23] The aad is thus 0.24 eV, which shows that the XPS spectrum is indeed compatible with the structure of untouched γ-APS. One can note a higher than usual ad for the O1s line, which we attribute to the molecular model, where the three (electron–donating)

Table I. Core-Electron Binding Energies (CEBEs, in eV) for the trihydroxy-form of γ-APS, γ-APS$(OH)_3$, compared with a tentative three-peak decomposition of the C1s region of spin-coated γ-APS. All values are referenced to the Fermi level of the spectrometer.[22)]

	Obs.(fit)[a]	Obs.(fit)-C_{rel}	DFT[b] (a.d.[c])
WD=4.66[d]			
$H_2N-CH_2CH_2CH_2-Si(OH)_3$	400.30	400.20	400.29 (0.09)
$H_2N-CH_2CH_2CH_2-Si(OH)_3$	286.70	286.65	286.65 (0.00)
$H_2N-CH_2CH_2CH_2-Si(OH)_3$	286.10	286.05	285.94 (0.11)
$H_2N-CH_2CH_2CH_2-Si(OH)_3$	285.50	285.45	285.45 (0.00)
$H_2N-CH_2CH_2CH_2-Si(OH)_3$	533.50	533.31	533.75 (0.44)
aad[e]			0.13

a. Ref.[22)]
b. uGTS with B88-P86/cc-pVTZ, present work.
c. Absolute deviation from experimental values, in eV.
d. This quantity (in eV) has been substracted from computed values to account for solid-state effects (see text).
e. Average absolute deviation from experiment, in eV.

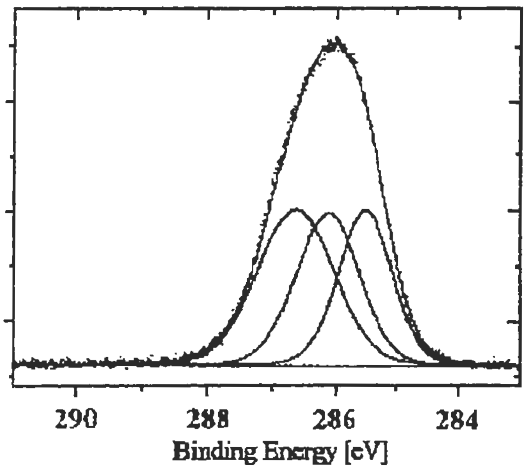

Fig. 4. C1s region of the XPS spectrum of a 30 nm thick film of γ-APS, spin-coated on a silicon wafer, and immediately introduced in the UHV analysis chamber. The tentative decompositions are those delivering the values of Table 1.

CH_2CH_3 groups on the oxygens have been rendered by hydrogen atoms.

When γ-APS is spin coated on a Si wafer and kept under the laboratory atmosphere, which contains H_2O and CO_2, additional components appear in its XPS spectrum, relative to that of native γ-APS[23)] : (i) one at 401.20 eV on the N1s line, in addition to the amine component of native γ-APS at 400.20 eV; (ii) two at 288.80 and 287.20 eV on the C1s line. In reference,[23)] George et al. make the hypothesis that within a H_2O/CO_2 atmosphere, the amine end of γ-APS undergoes a Brönsted acid-base reaction :

$$H_2N-CH_2-CH_2-CH_2-Si(OH)_3+H_2CO_3$$

$$\rightleftharpoons HCO_3^-+H_3N^+-CH_2-CH_2-CH_2-Si(OH)_3 \tag{3.1}$$

HCO_3^- and $H_3N^+-CH_2-CH_2-CH_2-Si(OH)_3$ being responsible for the 288.80 and 287.20 eV contributions on the C1s line and for the 401.20 eV component on the N1s line, respectively. We restrict our molecular model to the Methyl-Ammonium Hydrogen-Carbonate ion pair, $\{CH_3-NH_3^+, HCO_3^-\}$, to mimick the presumed N-protonated γ-APS.[22)] Let us first assume that the CEBEs of $CH_3-NH_3^+$ and HCO_3^- can be computed separately, i.e. as if the two ions could be taken as isolated systems. We see in Fig.5 that the resulting optimal aad is then 4.91 eV for the two ions considered as a whole, the corresponding WD being 11.75 eV. This aad is about 25 times as large as the agreement obtained with the uGTS procedure so far. Our second attempt is to let the $CH_3-NH_3^+$ and HCO_3^- ions actually come into interaction, hence considering the $\{CH_3-NH_3^+, HCO_3^-\}$ ion pair as a supermolecule. Two of the absolute deviations are too high by a factor of 5, eventhough the aad is much better, 0.72 eV, with a WD=6.48 eV. We have also examined whether farther intermolecular effects could be responsible for the discrepancy on the bare ion pair model. First, we have considered the "solvation" of the $\{CH_3-NH_3^+, HCO_3^-\}$ ion pair by an increasingly higher number of water molecules, giving $\{CH_3-NH_3^+, HCO_3^-; (H_2O)_n\}$, n=1-4, structures. Only $\{CH_3-NH_3^+, HCO_3^-; (H_2O)_4\}$ is depicted in Figure 6. These water molecules are meant to mimick : (i) either true water molecules which remain in the γ-APS film even after the solvent has been evaporated, in analogy with cristallization water in cristals; (ii) or OH groups from silanol ($Si(OH)_3$); (iii) or siloxane Si-O-Si groups resulting from an oligomerization of γ-APS molecules. The aads on CEBEs for all five $CH_3-NH_3^+, HCO_3^-; (H_2O)_n\}$, n=0-4, structures are shown in Figure 5, case 1 corresponding to the isolated ion attempt, case 2 to the bare ion pair, and cases 3 to

6 to n=1-4. We see that the overall optimal aad's are lowered from 0.72 eV to 0.31 eV in going from {CH_3-NH_3^+, HCO_3^-; $(H_2O)_0$} to {CH_3-NH_3^+, HCO_3^-; $(H_2O)_4$}, respectively (Fig.5), which indicates that polarization effects in the surroundings of the ion pair have a detectable effect - of the order of 0.4 eV - in the predicted CEBEs. A residual discrepancy exists between theory and experiment, since the highest deviation from experiment - the N1s CEBE for CH_3-NH_3^+ in {CH_3-NH_3^+, HCO_3^-; ($H_2O)_4$}- is of 0.45 eV.[22] We attribute this to the molecular model being too small and perhaps too imprecise. First, as polarization effects are obviously involved in the correct interpretation of experimental CEBEs, one can expect long-range effects (involving more than four neighbours as in the present study) to play a part in the electronic relaxation around this system. However, any further improvement towards aad's lower than 0.31 eV would only be meaningful upon actual consideration of silanol, siloxane or alcohol groups as neighbours. The present theory vs experiment comparison could well be applied to self-organised systems with benefit.

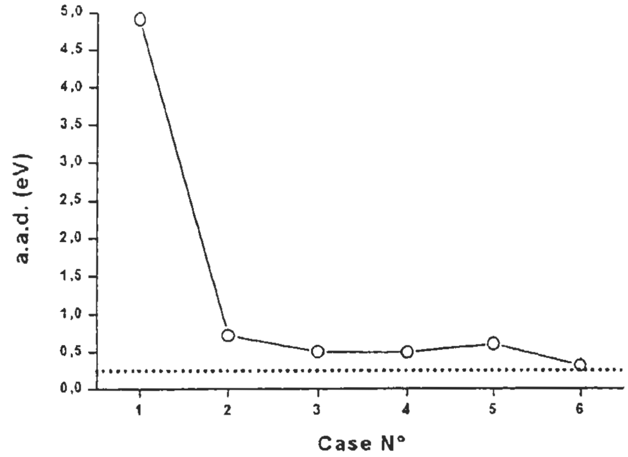

Fig. 5. Average absolute deviation with experiment of computed CEBEs (aad, in eV) as a function of the molecular model used to render the XPS spectrum of thermally treated γ-APS. Case 1 corresponds to isolated $CH_3NH_3^+$ and HCO_3^-; cases 2 to the bare {CH_3-NH_3^+, HCO_3^-} ion pair, and cases 3 to 6 to the solvated {CH_3-NH_3^+, HCO_3^-;$(H_2O)_n$} ion pairs, n=1-4 (cf Fig.6). Within each structures, the molecular geometries are optimized at the MP2/6-31G** level, while the relative geometry of the distinct molecules is optimized using the procedure of Claverie.[33, 34] The dotted line indicates the usual aad obtained with the DFT/uGTS procedure when the underlying molecular model is correct (aad≃0.25 eV).

3.2.2 Core XPS of CO chemisorbed on Pd(110) and Pd(100).

Let us now turn onto our DFT results on CO chemisorbed on Pd(100) and Pd(110). From the results gathered in Table 2, the aad's from experiment - using equation 1.11 - is 0.32 eV at the cc-pVTZ level, and 0.49 eV at the cc-pV5Z level. For comparison, the aad's obtained using the true ΔSCF approach are 1.49 and 1.05 eV with the same basis sets, respectively, i.e. two to five times higher than with our present method. We now wish to detail the content of these general trends. For Pd(100), the cc-pVTZ aad's are 0.96 eV if one supposes atop chemisorption and 0.18 eV if one supposes bridge chemisorption (Table 2). This result predicts that the observed values correspond to a bridge adsorption for CO on Pd(100), in agreement with previous works.[24] The corresponding cc-pV5Z aad's are 0.52 and 0.36 eV, and do not infirm the prediction. The results in Table 2 indicate that cluster-size effects seem to be reduced as compared to true ΔSCF calculations, with an aad of 0.16 eV for Pd_2CO and 0.20 eV for $Pd_4(100)$-CO (both at the cc-pVTZ level). These deviations are within experimental error, and thus can be considered as almost identical. For Pd(110), the cc-pVTZ aad's are 0.51 eV if one supposes atop chemisorption and 0.11 eV if one supposes bridge chemisorption (Table 2). Again, our results predict that the experimental results of ref.[24] correspond to a bridge chemisorption of CO on Pd(110). As with Pd(100), cluster-size has little influence on the computed CEBEs, with aad's of 0.16 eV (cc-pVTZ) to 0.30 eV (cc-pV5Z) for Pd_2CO and 0.06 eV (cc-pVTZ) to 0.42 eV (cc-pV5Z) for $Pd_4(110)$-CO. Thus, experimental CEBEs can be obtained using equation 1.11 with small metallic Pd clusters, within experimental error. One interesting test of our method is to examine and compare our predictions for the two (100) and (110) faces of the Pd surface. This test is all the more relevant as our two corresponding models, $Pd_4(100)$-CO and $Pd_4(110)$-CO, contain the same number of atoms. The two clusters identically comprise first nearest neighbours of the first and second atomic layers. The results of ref.[24] indicate that, when corrected for the work function of the two Pd faces, the O1s and C1s CEBEs are almost the same on both faces, i.e. 536.8 and 291.1 eV respectively, with an experimental precision estimated to be 0.1 eV.[24] Our present

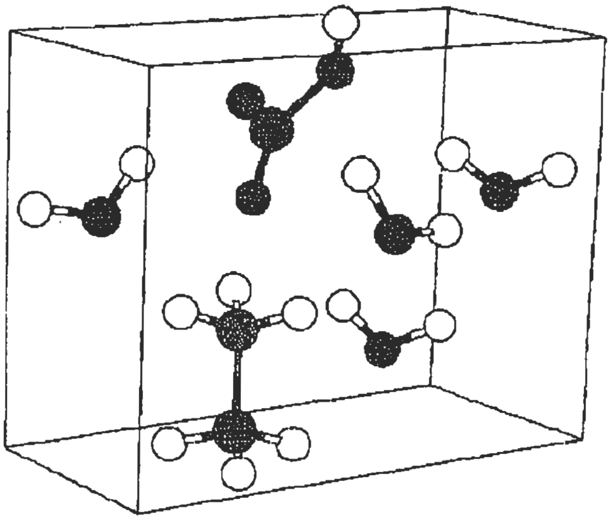

Fig. 6. Tridimensional molecular model of { $CH_3NH_3^+$,HCO_3^-; $(H_2O)_4$}, the bare ion pair solvated by four water molecules, as optimized with a simulated annealing + optimization procedure taking Van der Waals interactions into account (see text).[33, 34]

Table II. Theoretical *vs* experimental C1s and O1s CEBEs (in eV) for CO adsorbed on Pd(100) and Pd(110). The values in parenthesis indicate the absolute deviation (in eV) with respect to the experimental values. All calculated values are corrected for relativistic effects, and referenced to the vacuum.

Cluster	C1s[a]	C1s[a,d]	Exp.6)	O1s[a]	O1s[a,d]	Exp.6)
Atop						
Pd-CO[b,e]	293.96 (2.73)	292.75 (1.55)	291.20	539.96 (3.06)	538.79 (1.89)	536.90
Pd-CO[c,e]	293.60 (2.40)	292.39 (1.19)	291.20	539.28 (2.38)	538.33 (1.43)	536.90
Pd-CO[b,f]	293.96 (2.86)	292.30 (1.20)	291.10	539.96 (3.16)	538.33 (1.53)	536.80
Pd-CO[c,f]	293.60 (2.50)	291.94 (0.84)	291.10	539.28 (2.48)	537.88 (1.08)	536.80
Pd$_7$-CO6)	293.85 (2.75)	-	291.20	293.85 (2.75)	-	536.90
Bridge						
Pd$_2$-CO[b,e]	292.89 (1.69)	292.29 (1.09)	291.20	538.12 (1.22)	537.38 (0.48)	536.90
Pd$_2$-CO[c,e]	292.50 (1.30)	291.69 (0.49)	291.20	537.63 (0.73)	536.90 (0.00)	536.90
Pd$_2$-CO[b,f]	292.89 (1.89)	291.84 (0.84)	291.00	538.12 (1.32)	536.93 (0.13)	536.80
Pd$_2$-CO[c,f]	292.50 (1.50)	291.24 (0.24)	291.00	537.63 (0.83)	536.45 (0.35)	536.80
Pd$_4$(100)-CO[b]	-	291.73 (0.53)	291.20	-	536.68 (0.22)	536.90
Pd$_4$(100)-CO[c]	-	290.64 (0.56)	291.20	-	-	536.90
Pd$_3$(100)-CO6)	293.85 (2.65)	-	291.20	539.60 (2.70)	-	536.90
Pd$_4$(110)-CO[b]	-	291.14 (0.14)	291.00	-	536.79 (0.01)	536.80
Pd$_4$(110)-CO[c]	-	290.74 (0.26)	291.00	-	536.31 (0.49)	536.80
Pd$_4$(110)-CO6)	294.35 (3.35)	-	291.00	540.20 (3.40)		536.80

a. Present work.
b. DFT/cc-pVTZ level.
c. DFT/cc-pV5Z level.
d. Equation (1.2).
e. Pd(100) : the added work function in eq.(1.2) is 5.65 eV.
f. Pd(110) : the added work function in eq.(1.2) is 5.20 eV.

results at the cc-pVTZ level are 536.88 and 536.77 eV for the O1s lines on Pd$_4$(100)-CO and Pd$_4$(110)-CO, respectively, and 291.02 and 291.09 eV for the C1s lines on Pd$_4$(100)-CO and Pd$_4$(110)-CO, respectively. These results are in excellent agreement with experiment, which is remarkable since the two work functions we added in equation 1.11 are 5.65 eV for Pd(100) and 5.20 eV for Pd(110).26) Hence, the theory vs experiment agreement is indeed due to the first term in equation 1.11, which correctly describes the effect of nearest neighbours geometry on the resulting CEBEs. These results also suggest that one can directly get the CEBEs referenced to the Fermi level of the metallic sample by evaluating the excitation energies (first term in equation 1.11). This idea of focusing on excitation energies rather than true core-ionizations is physically more in line with what actually happens in a spectrometer, since the sample is meant to have its Fermi level adjusted to that of the apparatus. Our approach has the additional advantage that one may ignore the Fermi energy of the actual sample (just like in most experiments) and nonetheless compare theoretical with experimental values, provided that (i) there is no charging effect on the sample, and (ii) the low-coverage approximation leading to equation 1.11 is valid. An experimental cross-check of these two criteria can be obtained by comparing the XPS spectrum (referenced to the Fermi level of the spectrometer) and the XAS spectrum (X-ray Absorption Spectroscopy) of the same sample : as soon as points (i) and (ii) above are fulfilled, the peak energies should be the same. This is essentially the content of our equation 1.11 and of the approximations leading to it.

§4. Concluding remarks

The collection of results we have presented suggests that the accurate calculation of core-electron binding energies has now come to be an interesting alternative for the decomposition of XPS spectra on compounds for which there exists no gas-phase reference spectrum. With the present uGTS/DFT method, aad as low as 0.20 to 0.30 eV can be obtained quite systematically on organic compounds both in the gas phase and chemisorbed on metals, as soon as the underlying presumed molecular geometry is correct. This constitutes a significant improvement over previous theoretical approaches, and allows one to be more affirmative on the plausibility of molecular structures standing behind experimental XPS spectra. Upon relying on systematic aad's of the order of 0.2 eV, one may use the procedure as a stringent test, and bring out very detailed informations on the physicochemical environment felt by each and every atom in a molecule. In particular, the examples shown in the present review indicate that some intermolecular effects may be detectable using XPS, although the technique deals with core levels. The present results - concerned with ion-pairing and ion-dipole solvation effects - as well as others to be detailed elsewhere - dealing with hydrogen bonds - suggest that most electrostatic intermolecular effects may be responsible for shifts of the order of 0.4 to 0.7 eV, which is higher than the resolution of most experiments. This tool should find peculiar interest in the field of polymer and, in general, solid interfaces.

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Discussion with the refree

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— *reviewer's comments* —

The manuscript concerns a valuable review for accurate density functional calculation of core XPS spectra. Its novelty lies in the fact that the accurate calculation has come to be an interesting alternative for the decomposition of XPS spectra on compounds for there is no gas-phase reference spectrum. With the uGTS/DFT method, aad of 0.20 to 0.30 eV can be obtained quite systematically on organic compounds both in the gas phase and chemisorbed on metals.

My recommendation is that it would be published without revisions. A suggestion I would like to discuss is the following:

(1). For geometry optimization, I also think it is very profitable to use ab initio Hartree Fock SCF program using MP perturbation method with a little large basis set. Only by the deMon DFT program are we able to obtain similar results of CEBEs for single molecules and interaction cases such as chemisorption and so on, when we use it from the geometry optimizations to the SCF convergences of KS equation?

— *anser from author* —

As regards the referee's comments :

(1) This is an interesting remark. Of course, using larger basis sets usually constitutes an efficient and systematic way to improve molecular geometries. The alternative proposed by the referee is probably the best compromise between excellency and cpu time consumption. However, Professor Chong and myself have shown recently - on a number of selected examples - that XPS is not sensitive to the difference between geometries obtained at the DFT (deMon) MP2 levels. More precisely, the difference is that the average absolute deviation on the CEBEs is 0.2 and 0.15 eV, respectively (on the selected examples). As this aad is below the experimental resolution in most cases, this difference is thus irrelevant. Actually, we have shown that much poorer geometries - such as those obtained at the AM1 level - were still adequate, at least for polymers.