

Evidencing Intermolecular Effects with Core-Level Photoelectron Spectroscopy via the Accurate Density Functional Calculation of Core–Electron Binding Energies on Model Systems: γ -APS as a Test

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γ -Aminopropyltriethoxysilane (γ -APS) is a molecule which is used as an adhesion promoter in microelectronics, for the coating of oxidized silicon wafers with polyimide films. The Si/ γ -APS interface has been studied recently using X-ray photoelectron spectroscopy, and evidenced a need for reference spectra of both γ -APS and its thermal byproducts: as γ -APS oligomerizes readily upon warming, no gas phase, reference, or XPS spectrum of this compound can be obtained experimentally. Thus, spectral features emerging from Si/ γ -APS interactions are difficult to separate from structural fingerprints of γ -APS alone. This phenomenon further hinders the follow up by XPS of structural modifications the molecule undergoes upon thermal treatments. A recent procedure of computing very accurate core–electron binding energies (CEBEs) via density functional theory (DFT) is used as a guide to propose a pseudo reference spectrum. The computed CEBEs of the various core levels of the isolated molecule are found in excellent agreement with the experimental XPS spectra recorded upon spin coating the compound on a silicon wafer at room temperature, with an average absolute deviation (aad) for C 1s, N 1s, and O 1s levels of only 0.13 eV, i.e., of the order of experimental resolution. The same procedure is then conducted on isolated ionic structures presumably formed when thick γ -APS layers have undergone thermal treatment in a H₂O/CO₂ atmosphere. A very bad agreement is found between theory and experiment on these isolated ions, with aad's as large as 4.91 eV. Upon actually computing the CEBEs on larger molecular models in which (i) ions are paired and then in which (ii) ion pairs are further solvated by one up to four water molecules, the aad reduces to 0.31 eV. We suggest, on the instance of γ -APS, that (i) the accurate calculation of CEBEs has now come to be a tractable and reliable alternative as a hand for spectrum decomposition when gas-phase reference XPS spectra are not available for calibration and that (ii) the availability of an accurate and tractable theoretical procedure to compute CEBEs, compatible with experimental precision, enables XPS to give some information on intermolecular effects, although this spectroscopy involves core ionizations.

I. Introduction

Polyimides are commonly used as surface coatings on silicon wafers in microelectronics. 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, polyimides suffer from poor adhesion characteristics. To overcome this problem, adhesion promoters such as γ -aminopropyltriethoxysilane (γ -APS: H₂N–CH₂–CH₂–CH₂–Si(OCH₂CH₃)₃) are used to precondition the silicon substrates on which the polymer is deposited.^{1,2} The very mechanism of the interaction of γ -APS with actual silicon wafers is difficult to elucidate due to the complexity of the system, and a number of molecular models have been proposed for the molecular structures occurring at the Si/ γ -APS interface.³ These models rely on an analysis of experimental information obtained via infrared spectroscopy and X-ray photoelectron spectroscopy (XPS). In this last field, the C 1s, N 1s, O 1s,

and Si 2p 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 undergone by γ -APS can range from hydrogen bonds (–NH₂ groups) to true chemical bonds (surface and/or intermolecular Si–O–Si bridges) as well as ionic bonds (Si–O[–], ⁺H₃N–), which means that chemical shifts due to surface deposition or structural modifications can range from a fraction of an electronvolt to several electronvolts. 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 byproducts. In the present work, our first aim will consist in being able to point out whether observed XPS chemical shifts are intrinsic to the molecular structure or do result from intermolecular interactions. Our second aim will be to use this pseudo reference spectrum as a starting point to elucidate structural changes upon thermal treatment of spin-coated γ -APS

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under a H₂O/CO₂ atmosphere. The alternative we wish to propose is to make an accurate computation of the CEBEs of the γ -APS molecule. The procedure we use is based upon the unrestricted generalized transition state model (uGTS), recently proposed by Chong,^{5–7} that gives excellent results with an aad ≈ 0.15 . This procedure is thus capable of delivering computed CEBEs of experimental quality on known structures, with aad's which are of the order of experimental resolution (0.2 eV). In some instances, it could even confirm conformational attributions for structures separated by no more than 1 kcal/mol, such as in the case of the two lowest conformers of gas-phase glycine.⁸ We use this technique as a probe, i.e., the molecular structures we try to elucidate are those of a real system and are not precisely known. On the other hand, we decide to rely completely on the calculation procedure to help us scan various plausible structures mimicking the presumed structural changes. Thus, our strategy is the following: (i) we propose plausible molecular models and use our procedure to obtain predicted CEBEs, as our procedure is meant to be as precise as experiment, (ii) as soon as we have found the correct underlying molecular structures, we shall consider as nonplausible those molecular models which give too large discrepancy between theory and experiment. The experimental details corresponding to the present theoretical work have been given elsewhere.⁴ Let us simply recall that γ -APS was spin-coated (3000 rpm) from a 1 vol % solution in 95:5 (v/v) methanol/water solution on cleaned silicon wafers covered by a 20 Å thick native silicon oxide layer (as estimated by ellipsometry).⁴ The thickness of the γ -APS layer was about 30 nm (ellipsometry). Lowering down the concentration of γ -APS in the methanol/water solution did not permit to obtain layers thinner than 1–1.5 nm.⁴ The acquisition of XPS data was carried out with an Escalab 210 spectrometer using a monochromatized Al K α source (1486.6 eV).⁴ High-resolution spectra were corrected for charging effects by assigning a value of 99.15 eV to the Si 2p_{3/2} for a bare silicon wafer. Under these conditions, the saturated hydrocarbon C 1s level of contaminants was found at 285.0 eV.⁴

II. Calculations

A procedure was recently discovered by one of us to compute accurate CEBEs via density functional theory (DFT).^{5–7} This procedure has been tested on about a hundred of molecular systems ranging from small molecules (CO, CH₄, ... etc.) to larger models (n -unit models of polymers, $n = 1–3$),^{9–12} with an average absolute deviation equal to 0.23 eV.⁶ Our experience is that the results are even better on larger systems, with aad's as low as 0.15 eV.^{9,12} The procedure uses the unrestricted generalized transition-state (uGTS) model and an exchange-correlation potential labeled B88-P86, made from Becke's 1988 exchange¹³ and Perdew's 1986 correlation functionals.¹⁴ The uGTS model for ionization from Kohn–Sham orbital k approximates the nonrelativistic ionization energies by¹⁵

$$I_{nr} = \frac{1}{4} \left(\frac{\partial E}{\partial n_k} \right)_{n_k=n_k^0} + \frac{3}{4} \left(\frac{\partial E}{\partial n_k} \right)_{n_k=n_k^0-2/3} \quad (1)$$

where E is the Kohn–Sham electronic energy, n_k^0 is the occupation number of orbital k in the parent neutral molecule and n_k is the actual occupation number of orbital k . The value $n_k = n_k^0 - (2/3)$ represents a system in which a $2/3$ partial core–hole is forced into molecular orbital k , and on which full orbital relaxation is allowed. The partial derivatives in equation 1 are easily obtained via Janak's theorem as¹⁶

$$(\partial E / \partial n_k) n_{k,n_k^0-\lambda} = -\epsilon_k(\lambda) \quad (2)$$

where $\epsilon_k(\lambda)$ is the Kohn–Sham energy of molecular orbital k when λ electrons have been removed from this orbital. 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. In order to compare the calculated CEBEs with experiment, we need an evaluation of relativistic effects (which we will not take into account explicitly in the quantum mechanical treatment). A crude estimate of relativistic corrections can be made by subtracting from the experimental values the quantity:⁶

$$C_{rel} = K I_{nr}^N \quad (3)$$

where $K = 2.198 \times 10^{-7}$ and $N = 2.178$, when both I_{nr} and C_{rel} are in eV. The experimental values (corrected for relativistic effects) will be implicitly referenced to the Fermi level of the spectrometer used in our previous study.⁴ In order to account for solid-state effects, a quantity WD is subtracted from computed CEBEs.¹⁸ This quantity (WD) denotes the sum of the work function of the sample and other energy effects, such as the polarization energy, the width of the intermolecular band formation, and the peak broadening in the solid state. In the present work, the WD's were chosen so as to minimize the sum of the absolute average deviations from experiment.⁴ The DFT calculations were done with the deMon code¹⁹ on a Cray C94. The set of auxiliary basis functions is (5,4;5,4) for Si, (4,4;4,4) for C, N, and O and (3,1;3,1) for H.²⁰ The orbital basis sets are Dunning's correlation-consistent valence triple-zeta basis sets (cc-pVTZ) on Si, C, N, O, and H.²¹ As previously,⁷ scaled-pVTZ basis sets have been used on the partially ionized atomic centers in order to better describe the core–hole. 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 \times 194 angular points per atom. In the instance involving large bond distances, we have used the larger cc-pV5Z basis set with a grid comprising 64 \times 194 points per atom. The functionals are Becke's 1988¹³ for the exchange term and Perdew's 1986¹⁴ for the correlation term. As was done previously, preliminary calculations on isoelectronic species with fictitious nuclear charges (B[−] replacing C, etc.) were carried out in order to cope with the problem of core–hole localization in the ionized systems.^{9,10} As regards the geometry of the various systems, two distinct types of geometry optimizations were performed.

First, γ -APS(OH)₃ (Figure 1) used to model isolated γ -APS, CH₃NH₃⁺ (methylammonium; Figures 3 and 4) used to model the ammonium extremity of protonated γ -APS, HCO₃[−] (Figures 3 and 4) and H₂O molecules, used to mimic, the vicinal presence of OH or siloxane Si–O–Si oxygens in the vicinity of ion pairs, were all four optimized separately at the MP2/6-31G** level using the following procedure: the geometry is first optimized at the RHF/3-21G level, and then at the RHF/3-21G**, MP2/3-21G**, and MP2/6-31G** levels. At each level, the optimization was restarted using the geometry and Hessian of the previous step. The geometry optimizations were performed using the GAMESS code¹⁷ on a 128-node Cray T3D.

Second, models in which CH₃NH₃⁺, HCO₃[−], and several H₂O molecules are put into interaction—used to describe plausible structures of the thermal byproducts—were considered on the basis of their van der Waals interactions only. This is justified by the fact that these species are ionic or bear intense dipole

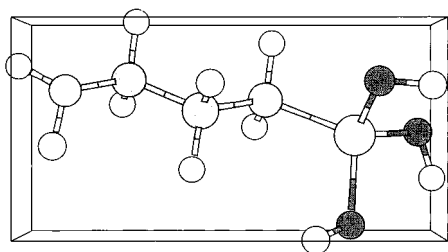


Figure 1. Molecular structure of γ -APS(OH)₃, the tri-hydroxy form of γ -APS, used to compute the CEBEs of Table 1. The detailed formula is $\text{H}_2\text{N}-\text{CH}_2\text{CH}_2\text{CH}_2-\text{Si}(\text{OH})_3$.

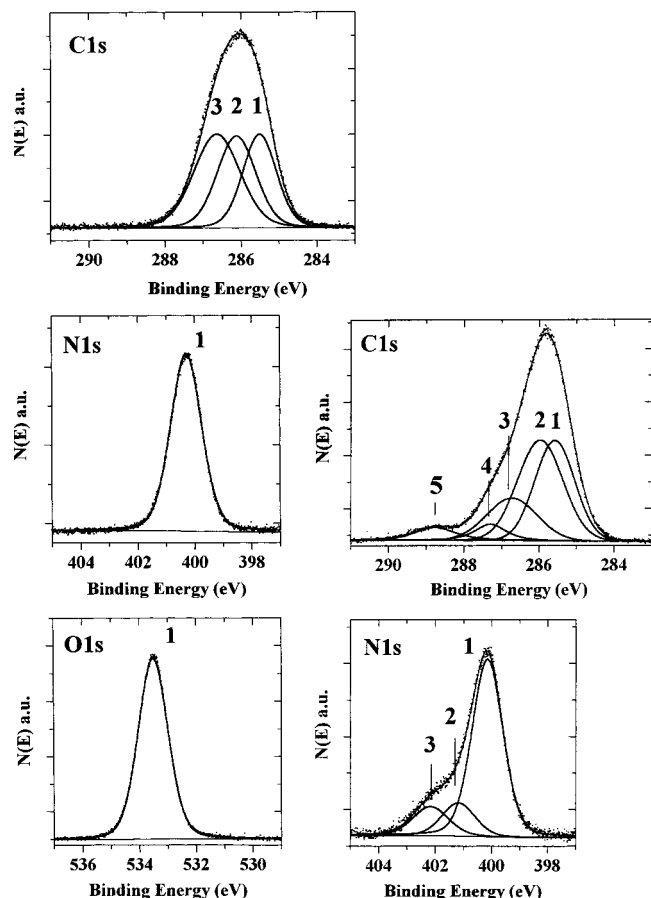


Figure 2. (a, left) C 1s, O 1s, and N 1s regions of the XPS spectrum of a 30 nm thick film of γ -APS, spin-coated on a silicon wafer, and immediately introduced in the UHV analysis chamber. The tentative decompositions are those delivering the values of Table 1. (b, right) C 1s and N 1s lines of the same sample kept for 2 days at ambient atmosphere. Those C 1s lines labeled 1–3 have the same binding energy as in (a), while lines 4–5 are new lines. The N 1s line labeled 1 has the same binding energy as in (a), while lines 2–3 are new lines.

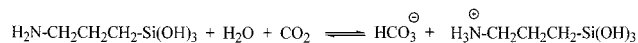


Figure 3. Sketch of the Brönsted acid–base reaction which is thought to occur upon thermally treating a film of γ -APS under a $\text{H}_2\text{O}/\text{CO}_2$ atmosphere.

moments. We thus expect their interactions to be well reproduced by semiempirical interaction potentials. In each case, the internal geometry of each fragment is kept at the isolated MP2/6-31G** geometry. Multipolar expansions of the electronic density are first obtained by fitting the MP2/6-31G** density of each fragment, according to the procedure of Claverie.²² The electrostatic component of the interaction potentials is computed directly from these expansions, by taking the atoms plus one point on each bond as centers and keeping

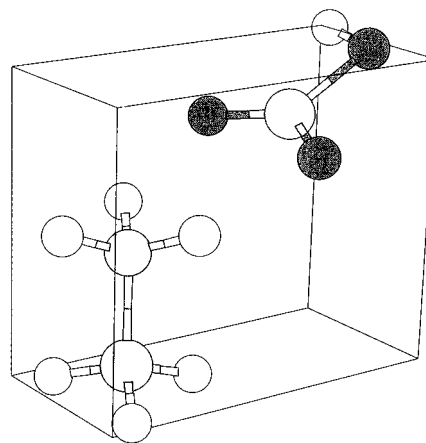


Figure 4. Tridimensional molecular model of $[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-]$, the ion pair formed between methylammonium (CH_3NH_3^+ , left) and the hydrogen carbonate anion (HCO_3^- , right), as optimized with a simulated annealing + optimization procedure taking van der Waals interactions into account (see text).

up to quadrupole terms, while polarization, dispersion and repulsion terms are accounted for by semiempirical expressions.²³ The polarization term is obtained by summing the polarization energies of each molecular subunit due to the electric field created by the multipoles of all others molecular subunits. That is done at the second-order perturbation level, which leads to n -body terms and requires the knowledge of multipolar distributions as well as experimental polarizability values.²³ The dispersion and repulsion contributions are both sums of atom–atom terms: the dispersion energy includes terms up to C_{10}/R_{ij}^{10} ; the latter contribution takes into account the electronic population variation of each atom of the molecule and its influence on the van der Waals radius.²³

The potential energy hypersurfaces, giving the interaction energies as a function of the various relative coordinates (intermolecular distances and Euler angles) are first scanned using a simulated annealing approach.²² The relative coordinates of the resulting candidates are then optimized, and the structures are sorted in order of increasing interaction energy. Only those ranging within kT from the lowest structure (typically, this represents about 10 different geometries) are kept to compute the CEBEs. In this way, we are sure to examine all possible relevant minima.

III. Proposing a Reference Spectrum for γ -APS

In this section, we detail the theoretical results obtained on the trihydroxy form of γ -APS ($\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OH})_3$, Figure 1), which will be termed γ -APS(OH)₃ from now on. The three carbons of the γ -APS backbone (Figure 1) are not resolved in the C 1s region of the XPS spectrum of the 30 nm thick film of γ -APS deposited on the silicon wafer (Figure 2).⁴ However, the observed peak obviously stems from several contributions, as suggested by the full width at half-maximum (fwhm) of 2.5 eV.⁴ 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, which would suggest three peaks (resulting fwhm’s \approx 1.35 eV). In this last case, however, it is the structure of the molecule which serves to interpret the XPS spectrum. This reduces considerably the a priori analytical power of the technique, and, in short, its interest, when trying to follow in situ the physicochemical modifications of the original system. We have thus computed the CEBEs of γ -APS(OH)₃, focusing on the resolution that may be expected on the C 1s line. The results of the calculations

TABLE 1: 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 C 1s Region of Spin-Coated γ -APS (cf. Figure 2)^a

	obs obs (fit) ^b	(fit) – C_{rel}	DFT ^c (a.d. ^d)
WD = 4.66 ^e			
H ₂ N–CH ₂ CH ₂ CH ₂ –Si(OH) ₃	400.30	400.20	400.29 (0.09)
H ₂ N–CH ₂ CH ₂ CH ₂ –Si(OH) ₃	286.70	286.65	286.65 (0.00)
H ₂ N–CH ₂ CH ₂ CH ₂ –Si(OH) ₃	286.10	286.05	285.94 (0.11)
H ₂ N–CH ₂ CH ₂ CH ₂ –Si(OH) ₃	285.50	285.45	285.45 (0.00)
H ₂ N–CH ₂ CH ₂ CH ₂ –Si(OH) ₃	533.50	533.31	533.75 (0.44)
aad ^f			0.13

^a All values are referenced to the Fermi level of the spectrometer.⁴^b Reference 4. ^c uGTS with B88-P86/cc-pVTZ, present work. ^d Absolute deviation from experimental values, in eV. ^e This quantity (in eV) has been subtracted from computed values to account for solid-state effects (see text). ^f Average absolute deviation from experiment, in eV.

are shown in Table 1, together with the tentative three-peak decomposition of the C 1s region of the spectrum displayed in Figure 2. We remark that the calculated CEBEs for the three carbons in γ -APS(OH)₃ are more than 0.50 eV apart. Thus, the three methylene groups in γ -APS can, in principle, be resolved using spectrum decomposition. A tentative mathematical three-peak fit is performed on the spectrum displayed in Figure 2, giving the peak energies shown in Table 1, with respective fwhms of the order of 1.30 eV.⁴ One sees that the agreement is very good between experimental peak energies and computed CEBEs, for the C 1s as well as for the N 1s levels, with an average absolute deviation of only 0.13 eV, with WD = 4.66 eV. The absolute deviation is larger than the expected precision of our method (0.44 eV vs ca. 0.2 eV) for the O 1s level. We attribute this to the fact that we have modeled γ -APS with its trihydroxy form and that we have compared the computed values with the results obtained on a spin-coated sample. First, in the true γ -APS molecule, oxygen atoms are involved in ether links with ethanol molecules. Second, it is quite well established¹ that γ -APS undergoes an oligomerization in the vicinity of oxidized silicon wafers, with the formation of Si–O–Si bridges and the elimination of one or more ethanol molecule(s) (CH₃CH₂OH): hence, the actual chemical environment of a typical oxygen atom is Si–O–Si or Si–O–CH₂– rather than Si–O–H. In both cases, we predict that taking the actual chemical environment up to the first neighbors will lower the CEBEs, which is consistent with our present CEBEs for the O 1s levels being too high. Hence, the C 1s broad line in Figure 2 can, to our point, be safely decomposed on the basis of three peaks corresponding to each carbon center of the γ -APS molecular skeleton.⁴

IV. Insight into Thermal Byproducts

In this section, we try to follow the structural changes of molecular byproducts following exposure of γ -APS to atmosphere (i.e., H₂O/CO₂), by examining several molecular models to account for the observed XPS spectra. Experimentally, the main spectral changes are (i) the appearance of a large high-energy shoulder on the N 1s line, which was tentatively decomposed in two components at 402.20 and 401.20 eV (Fermi level reference), respectively, in addition to the amine line at 400.20 eV (Figure 2); (ii) modifications in the high-energy side of the C 1s line, with new components at 288.80 and 287.20 eV (Fermi level reference), which correspond to carbons in a highly electronegative environment.⁴ In ref 4, George et al. make the hypothesis that within a H₂O/CO₂ atmosphere, the amine end of γ -APS undergoes a Brønsted acid–base reaction

TABLE 2: N 1s and C 1s Core–Electron Binding Energies (CEBEs, in eV) for Methylamine, Methylammonium, Hydrogen–Carbonate, and Methylamine Interacting with Carbonic Acid (See Text)^a

	obs obs (fit)	(fit) – C_{rel}	scaled-pVTZ ^b (a.d. ^c)	cc-pV5Z ^b (a.d. ^c)
WD = 4.50 ^d				
CH ₃ NH ₂	287.10 ^e	287.05	287.12 (0.07)	
CH ₃ NH ₂	400.60 ^e	400.49	400.42 (0.07)	
aad ^f			0.07	
WD = 11.75 ^d				
CH ₃ NH ₃ ⁺	401.20 ^g	401.10	404.09 (2.99)	
HCO ₃ [–]	288.80 ^g	288.75	277.11 (11.64)	
CH ₃ NH ₃ ⁺	287.20 ^g	287.15	287.04 (0.11)	
aad ^f			4.91	
WD = 5.19 ^d				
CH ₃ NH ₂ , H ₂ CO ₃	401.20 ^g	401.10	400.54 (0.56)	400.52 (0.58)
CH ₃ NH ₂ , H ₂ CO ₃	288.80 ^g	288.75	289.72 (0.97)	
CH ₃ NH ₂ , H ₂ CO ₃	287.20 ^g	287.15	286.82 (0.33)	
aad ^f			0.65	

^a The experimental CEBEs are those corresponding to the decomposition of the XPS spectrum of γ -APS after atmospheric exposure.⁴All values are referenced to the Fermi level of the spectrometer.⁴^b uGTS with B88-P86/scaled-pVTZ or B88-P86/cc-pV5Z, present work.^c Absolute deviation from experiment, in eV. ^d This quantity (in eV)has been subtracted from computed values to account for solid-state effects (see text). ^e Reference 9. ^f Average absolute deviation from experiment, in eV. ^g Reference 4. The attributions are tentative and

constitute the most plausible propositions.

(Figure 3). This would lead to the formation of hydrogen carbonate anions, HCO₃[–], and γ -APS(OH)₃ ammonium ends, H₃N⁺CH₂CH₂CH₂Si(OH)₃, responsible for the 288.80 and 287.20 eV contributions on the C 1s line and for the 401.20 eV component on the N 1s line, respectively, while the 402.20 eV component would be due to Brønsted type reactions with Si–OH groups from γ -APS (to form ammonium silicate ion pairs).⁴ In the present paper, we focus our attention onto the Brønsted reactions with H₂O/CO₂, i.e., we leave the 402.20 eV component in Figure 2b for a forthcoming paper. Since the major expected modification is the protonation of the amine end of γ -APS (Figures 3 and 4), we focus our attention on the spectral modifications noticed on the N 1s line of native spin-coated γ -APS.⁴ At the theoretical level, we restrict our molecular model to the methylammonium hydrogen carbonate ion pair (Figure 4) to mimic the presumed N-protonated γ -APS. As a mere control, we mention in Table 2 the computed N 1s CEBEs of methylamine: we obtain a value (400.42 eV) which is in quite close to the one obtained in γ -APS(OH)₃ (400.45 eV). Therefore, we shall first estimate that the aliphatic and silanol part of γ -APS does not interfere with the ionic pairs formed on the amine end, at least as regards the resulting XPS spectrum. We also see that both C 1s (287.12 eV) and N 1s (400.42 eV) CEBEs are in excellent agreement with reference lines available for methylamine: the aad is of 0.07 eV.⁹

Let us first assume that the CEBEs of CH₃NH₃⁺ and HCO₃[–] can be computed separately, i.e., on CH₃NH₃⁺ and HCO₃[–] taken as isolated systems. We see in Table 2 that the corresponding absolute deviations are of 0.11 and 2.99 eV for the C 1s and N 1s lines of CH₃NH₃⁺, respectively, and of 11.64 eV for the C 1s line meant to correspond to HCO₃[–]. The resulting optimal aad is then 4.91 eV for the two ions considered as a whole (Table 2), with WD = 11.75 eV. This aad is about 25 times as large as the agreement obtained with the uGTS procedure so far. Moreover, the value of WD found in this case, which should be somewhat related to the work function of the sample, is too large for a sample which did not show any charging effect. It is thus obvious that this independent ions model is inconsistent with the actual system which is detected via spectroscopy

measurements, and the molecular model itself needs to be reconsidered in order to understand what we have missed.

Our second attempt was to let the CH_3NH_3^+ and HCO_3^- ions actually come into interaction (Figure 4). We used the simulated annealing plus optimization method described in section 2²² to obtain a workable geometry for this bimolecular system, and determined the most stable configurations. The computed CEBEs are shown in Table 2. The C 1s CEBE of HCO_3^- (287.66 eV) now deviates by 1.09 eV with respect to experiment, which constitutes an interesting result. For CH_3NH_3^+ , the computed C 1s CEBE (287.15 eV) exactly matches the experimental value, but the computed N 1s CEBE (402.18 eV) has an absolute deviation from experiment of 1.09 eV. Two of the absolute deviations are thus too high by a factor of 5, even though the aad is much better, 0.72 eV (Table 2). The WD parameter (6.48 eV) is fairly far from the original work function of the spectrometer (4.50 eV) and is hardly compatible with weak charging effects. This alludes to these ionic compounds as interesting candidates, but for which further insights are needed. We shall return later to this point.

Our subsequent attempt was to examine whether the approximation of using frozen geometries for the CH_3NH_3^+ and HCO_3^- fragments in the interacting ion pair was sustainable. We have thus taken the optimized geometry obtained with the simulated annealing plus optimization procedure and used it as a starting point for a full ab initio geometry optimization at the MP2/6-31G** level. During the course of the optimization, a proton initially belonging to the ammonium end of CH_3NH_3^+ is transferred to HCO_3^- , hence giving $\text{CH}_3\text{NH}_2 + \text{H}_2\text{CO}_3$. This proton transfer comes from the fact that the optimization is carried out without taking solvent effects into account. This gas phase calculation leads to the prediction that the neutral molecular pair is more stable than the ion pair, although the reverse situation would certainly be obtained upon actually taking solvation effects into account. Upon freezing NH distances in the original $\text{CH}_3\text{NH}_3^+ + \text{HCO}_3^-$ structure, geometrical relaxations are very small and lead to essentially the same CEBEs as with the simulated annealing + optimization procedure alone. Alternatively, the CEBEs of the $\text{CH}_3\text{NH}_2 + \text{H}_2\text{CO}_3$ structure are given in Table 2. Since carbonic acid H_2CO_3 is unstable and readily dissociates back to H_2O and CO_2 in acidic medium, this structure rather corresponds to methylamine in the presence of CO_2 , with a water molecule in the vicinity. The CEBEs for the N 1s of methylamine (400.54 eV), the C 1s of methylamine (286.82 eV), and the C 1s of CO_2 with proximal H_2O (289.72 eV) deliver an aad of 0.65 eV. One can note that the N 1s CEBE of methylamine is higher in the present interacting fragment (400.54 eV) as compared to isolated methylamine with the same WD (399.73 eV; the value in Table 2 is that with WD = 4.50 eV), evidencing a nonnegligible electron withdrawing effect of vicinal CO_2 and H_2O molecules on the amine end, although the interaction mainly involves hydrogen bonds. As a mere control, we have also carried out the calculation of the N 1s CEBE of methylamine interacting with $\text{H}_2\text{O}/\text{CO}_2$, using the much larger cc-pV5Z basis set. The N 1s CEBE is calculated to be 400.56 eV, which is quite close to the value obtained with the smaller scaled-pVTZ (400.54 eV). Thus, basis set effects can be neglected in the above results, and the shift in the N 1s CEBE in going from isolated methylamine to methylamine interacting with $\text{H}_2\text{O}/\text{CO}_2$ points to an actual detection of intermolecular effects on this N 1s CEBE. Alternatively, the C 1s CEBE of methylamine in the interacting fragment (286.82 eV) is pretty close to the one of isolated methylamine once corrected to use identical WD (286.43 eV; the value in Table 2 is that with WD = 4.50 eV).

This suggests that the interaction between $\text{CO}_2/\text{H}_2\text{O}$ with methylamine essentially involves the amine end and that farther fragments of the γ -APS molecule (CH_2 and silanol groups) should even be less affected. Hence, the hypothesis of the mere dissolution of CO_2 and H_2O within the γ -APS film thermally treated under a $\text{H}_2\text{O}/\text{CO}_2$ atmosphere is plausible, as far as CEBEs of the resulting structures are concerned. This hypothesis is rather trivial, and we now wish to gain further insights into the ion pair structures mentioned above, in order to ascertain whether they can be rejected.

As mentioned in the Introduction section, we keep on using the uGTS procedure as a probe, and rather consider more complicated systems which would account for the lower CEBEs observed experimentally on the γ -APS fragment, and the higher CEBE attributed to HCO_3^- .⁴ Just as we have evidenced it with systems involving methylamine and $\text{H}_2\text{O}/\text{CO}_2$, we have examined whether intermolecular effects are capable of delivering favorable aad's on the ion pair model. First, we have considered the "solvation" of the $[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-]$ ion pair by an increasingly higher number of water molecules, giving the $[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-; (\text{H}_2\text{O})_n]$, $n = 1-4$, structures depicted in Figures 5-8. These water molecules are meant to mimic (i) true water molecules which remain in the γ -APS film even after the solvent has been evaporated, in analogy with crystallization water in crystals or (ii) OH groups from silanol ($\text{Si}(\text{OH})_3$) or alcohol ($\text{CH}_3\text{CH}_2\text{OH}$) functions of vicinal fragments resulting from the hydrolysis of γ -APS or (iii) siloxane $\text{Si}-\text{O}-\text{Si}$ groups resulting from an oligomerization of γ -APS molecules. All these groups have in common that they bear an oxygen atom, the lone pairs of which are capable of acting as Lewis bases toward the ammonium end of protonated γ -APS (hence lowering its N 1s CEBE), while acting as a Lewis acid toward HCO_3^- , and hence lowering its C 1s CEBE as well. From this point of view, we feel that modeling the above compounds with water molecules is an acceptable attempt. In all cases, the relative geometry of all interacting fragments is the one of lowest energy as from the simulated annealing + optimization procedure. On the instance of $[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-; (\text{H}_2\text{O})_1]$, we have noticed that the various structures which energy ranged within kT from the lowest conformation only differed by the orientation of the water molecule with respect to heavier fragments. In short, the relative positions of heavy atoms (C, N, O) are not changed from one equilibrium conformation to the other, which gives essentially the same CEBEs for those heavy elements we are interested in. The CEBEs for all five $[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-; (\text{H}_2\text{O})_n]$, $n = 1-4$, structures are given in Table 3, and summarized graphically in Figure 9. These results show that computed CEBEs get closer and closer to experimental values as the number of water molecules increases, while deviating by more than 0.3 eV even with the $[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-; (\text{H}_2\text{O})_4]$ system. We see that the overall optimal aad's are lowered from 0.72 eV to 0.50, to 0.49, to 0.60, and to 0.31 eV in going from $[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-; (\text{H}_2\text{O})_0]$ to $[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-; (\text{H}_2\text{O})_4]$, respectively (Table 3, Figure 9). In the meanwhile, the WD parameter used to minimize the aad's lowers from 6.48 eV to 6.13, to 5.91, to 5.78, and to 5.73 eV, respectively (Table 3). As shown in Figures 5-8, the H_2O molecules tend to surround the CH_3NH_3^+ cation and keep closer to the nitrogen atom than any other, while their hydrogen atoms point toward the HCO_3^- anion. Thus, the water molecules are ideally oriented to raise the electron density around the ammonium nitrogen (which lowers its N 1s CEBE), while withdrawing electrons from the HCO_3^- anion thanks to the hydrogen bonds (which raises its C 1s CEBE as compared to the isolated ion pair, see Table 3). The lowest WD parameter, WD = 5.73 eV, is obtained with

TABLE 3: N 1s and C 1s Core–Electron Binding Energies (CEBEs, in eV) for $[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-; (\text{H}_2\text{O})_n]$, $n = 1-4$ (Figures 5–8), and $[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-]_2$ (Figure 10)^a

	obs (fit)	obs (fit) – C_{rel}	scaled-pVTZ ^b (a.d. ^c)
WD = 6.48 ^d			
$\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-$	401.20 ^e	401.10	402.18 (1.06)
$\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-$	288.80 ^e	288.75	287.66 (1.09)
$\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-$	287.20 ^e	287.15	287.15 (0.00)
aad ^f			0.72
WD = 6.13 ^d			
$[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-; \text{H}_2\text{O}]$	401.20 ^e	401.10	401.85 (0.75)
$[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-; \text{H}_2\text{O}]$	288.80 ^e	288.75	288.02 (0.73)
$[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-; \text{H}_2\text{O}]$	287.20 ^e	287.15	287.12 (0.03)
aad ^f			0.50
WD = 5.91 ^d			
$[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-; (\text{H}_2\text{O})_2]$	401.20 ^e	401.10	401.61 (0.51)
$[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-; (\text{H}_2\text{O})_2]$	288.80 ^e	288.75	288.01 (0.74)
$[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-; (\text{H}_2\text{O})_2]$	287.20 ^e	287.15	287.39 (0.24)
aad ^f			0.49
WD = 5.73 ^d			
$[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-; (\text{H}_2\text{O})_3]$	401.20 ^e	401.10	401.72 (0.62)
$[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-; (\text{H}_2\text{O})_3]$	288.80 ^e	288.75	287.85 (0.90)
$[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-; (\text{H}_2\text{O})_3]$	287.20 ^e	287.15	287.42 (0.27)
aad ^f			0.60
WD = 5.78 ^d			
$[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-; (\text{H}_2\text{O})_4]$	401.20 ^e	401.10	401.55 (0.45)
$[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-; (\text{H}_2\text{O})_4]$	288.80 ^e	288.75	288.77 (0.02)
$[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-; (\text{H}_2\text{O})_4]$	287.20 ^e	287.15	286.68 (0.47)
aad ^f			0.31
WD = 6.04 ^d			
$[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-]_2$	401.20 ^e	401.10	401.58 (0.48)
$[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-]_2$	288.80 ^e	288.75	288.40 (0.35)
$[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-]_2$	287.20 ^e	287.15	287.15 (0.00)
$[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-]_2$	401.20 ^e	401.10	401.59 (0.49)
$[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-]_2$	288.80 ^e	288.75	288.40 (0.35)
$[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-]_2$	287.20 ^e	287.15	286.89 (0.26)
aad ^f			0.32

^a The experimental CEBEs are those corresponding to the decomposition of the XPS spectrum of γ -APS after atmospheric exposure.⁴ All values are referenced to the Fermi level of the spectrometer.⁴

^b uGTS with B88-P86/scaled-pVTZ or B88-P86/cc-pV5Z, present work.

^c Absolute deviation, in eV. ^d This quantity (in eV) has been subtracted from computed values to account for solid-state effects (see text).

^e Reference 4. The attributions are tentative and constitute the most plausible propositions. ^f Average absolute deviation from experiment, in eV.

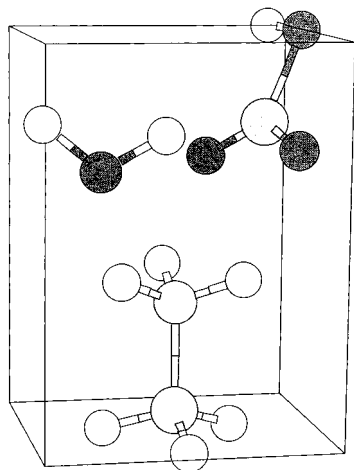


Figure 5. Tridimensional molecular model of $[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-; \text{H}_2\text{O}]$, the ion pair of Figure 4 solvated by one water molecule, as optimized with a simulated annealing + optimization procedure taking van der Waals interactions into account (see text).

$[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-; (\text{H}_2\text{O})_4]$ and still deviates by 1.23 eV from the original work function of the spectrometer (4.50 eV). Although the work function of the sample is indeed detected to

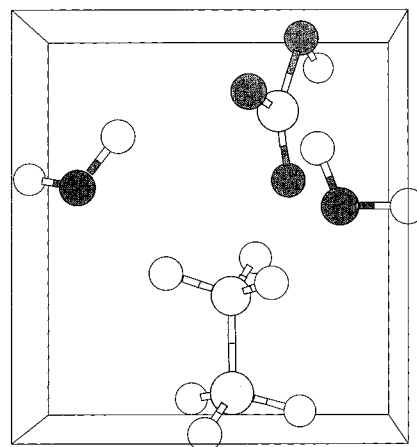


Figure 6. Tridimensional molecular model of $[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-; (\text{H}_2\text{O})_2]$, the ion pair of Figure 4 solvated by two water molecules, as optimized with a simulated annealing + optimization procedure taking van der Waals interactions into account (see text).

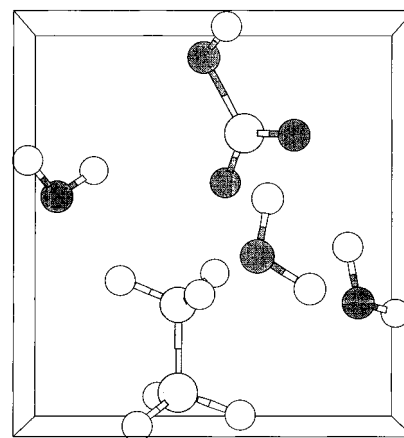


Figure 7. Tridimensional molecular model of $[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-; (\text{H}_2\text{O})_3]$, the ion pair of Figure 4 solvated by three water molecules, as optimized with a simulated annealing + optimization procedure taking van der Waals interactions into account (see text).

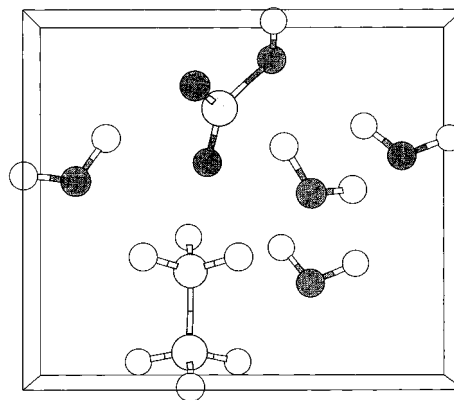


Figure 8. Tridimensional molecular model of $[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-; (\text{H}_2\text{O})_4]$, the ion pair of Figure 4 solvated by four water molecules, as optimized with a simulated annealing + optimization procedure taking van der Waals interactions into account (see text).

shift, experimentally, upon thermally treating the spin-coated γ -APS film,⁴ the shift is not as large as the above value, which suggests a residual discrepancy between theory and experiment that we attribute to the molecular model being too small and perhaps too imprecise. First, as Coulombic interactions are involved in the ion pair, one can expect long-range effects to play a part in the electronic relaxation around this system. Second, the above results indicate that our uGTS procedure is

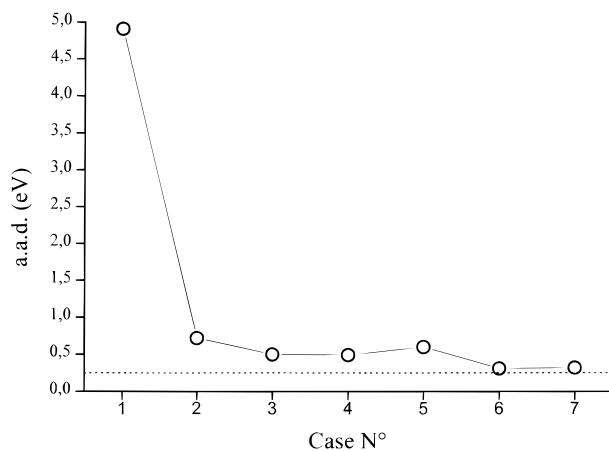


Figure 9. Average absolute deviation with experiment of computed CEBEs (aad, in eV) as a function of the molecular model used to render the XPS spectrum of thermally treated γ -APS. Case 1 corresponds to isolated CH_3NH_3^+ and HCO_3^- ; cases 2–6 correspond to the molecular models displayed in Figures 4–8, and case 7 corresponds to Figure 10. The dotted line indicates the usual aad obtained with the DFT/uGTS procedure when the underlying molecular model is correct (aad ≈ 0.25 eV).

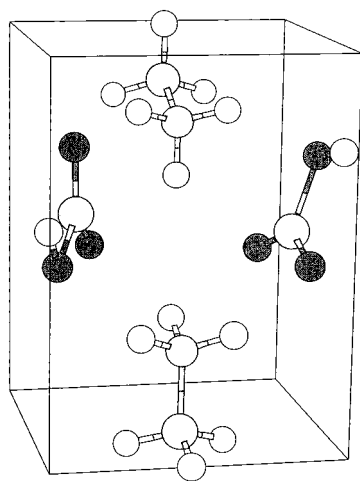


Figure 10. Tridimensional molecular model of $[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-]_2$, a cluster made with two ion pairs (Figure 4), as optimized with a simulated annealing + optimization procedure taking van der Waals interactions into account (see text).

capable of delivering a very detailed interpretation of XPS spectra in terms of molecular models, the best present aad being 0.31 eV. This is the best theory vs experiment agreement obtained in the present work. This suggests that the main part of the phenomenon responsible for those experimental CEBEs examined in this paper (ion pairing + interaction with vicinal oxygenated fragments) has been correctly understood. Any further improvement toward aad's lower than 0.31 eV would only be meaningful upon actual consideration of silanol, siloxane, or alcohol groups as neighbors.

One last attempt was nonetheless devoted to the study of the premisses of molecular self-assembly, by considering a cluster of two ion pairs, without water molecules: $[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-]_2$. This system was examined because we noticed that the largest improvement of the theory vs experiment agreement had been obtained by first pairing CH_3NH_3^+ with HCO_3^- . It could thus be that forming two ion pairs simultaneously would benefit even more to the lowering of the various CEBEs. The $[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-]_2$ structure is displayed in Figure 10, and the corresponding CEBEs are shown in Table 3. The optimal overall aad is 0.32 eV, obtained with $\text{WD} = 6.04$ eV. This is

about as good as the result obtained with four water molecule solvating a sole ion pair, and thus also constitute a plausible structure to account for experimental results. In $[\text{CH}_3\text{NH}_3^+, \text{HCO}_3^-]_2$, each CH_3NH_3^+ cation has two HCO_3^- anions as neighbors, which can act as Lewis bases toward CH_3NH_3^+ and lower its N 1s CEBE. Alternatively, each HCO_3^- anion has two CH_3NH_3^+ cations as neighbors, which can act as Lewis acids and raise its C 1s CEBE.

V. Concluding Remarks

The present paper shows, on the instance of γ -APS, that the accurate calculation of core-electron binding energies is an interesting alternative for the decomposition of XPS spectra on compounds for which there exists no gas-phase reference spectrum. We have modeled γ -APS through its trihydroxy form (γ -APS(OH)₃) and considered the mimicking of a condensed phase (γ -APS spin-coated on a Si wafer), perhaps self-assembled, by an isolated molecule. This model is relevant as long as intermolecular effects are not too important (and it looks as if they were not, from our average theory vs experiment agreement of 0.13 eV). The assumption we have tested is thus whether γ -APS has kept its overall chemical composition and was not chemically dissociated on the surface. Of course, the structure of the γ -APS layer is probably dependent on the actual substituent on the OH groups, but it has apparently no interference on the XPS spectrum. This would indicate that XPS is blind in detecting intermolecular effects, which is understandable in terms of the ratio of intermolecular energies to experimental resolution. This interesting result is not true in the second part of our paper, where ionic structures are involved. This is illustrated on the methylammonium hydrogen carbonate ion pair models, which constitute a sound basis for relating spectral changes with structural modifications obtained when γ -APS is thermally treated under a $\text{H}_2\text{O}/\text{CO}_2$ atmosphere. In particular, we have shown that intermolecular effects can be separated from intrinsically structural effects and help orient the interpretation of spectral modifications accompanying morphological and/or structural changes. To our knowledge, it is the first time that XPS is alluded to as a technique to evidence intermolecular effects. This proposal, if confirmed, could become an invaluable tool in fields such as the study of the morphology of polymers. This unexpected result is probably related to the peculiar system we have studied (the thermal byproducts of γ -APS), since ionic interactions are involved which give rise to spectral shifts of more than 1 eV. However, we have shown that ion pairing alone cannot deliver aad's lower than about 0.70 eV, and that interactions with at least second nearest neighbors are mandatory to lower the aad to about 0.30 eV (either in the form of clusters of ion pairs or in the form of "solvated" ion pairs). This suggests that these intermolecular effects, which should involve purely Coulombic and polarization terms, can be responsible for shifts of as high as 0.4–0.5 eV and gives experimentalists an order of magnitude of what may be looked for when dealing with charged species in condensed phases.

The very detailed nature of our predictions owes much to the virtues of the DFT/uGTS procedure discovered by Chong, which systematically delivers aad's of the order of 0.20 eV as soon as the molecular model is close enough from the actual structure. Moreover, the fact that this procedure makes use of DFT leaves much hope toward applying it to large systems at manageable computational effort. Further improvements and testings may be obtained as more is known on the tridimensional arrangements of the system under study. This will probably not be the case in the near future as regards the present γ -APS/

Si assembly, but the present theory vs experiment comparison could well be applied to self-organized systems with benefit.

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