

Ab Initio Theoretical Study of Substituted Dicarboxylic Acids Adsorbed on GaAs Surfaces: Correlation between Microscopic Properties and Observed Electrical Behavior

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Five substituted tartaric acid derivatives are studied using density functional theory, both isolated and adsorbed onto an oxidized GaAs cluster, to model molecular layers on semiconductor surfaces. The structures, energies, and electronic properties are computed to clarify the interactions responsible for the electric behavior of the modified surfaces, used in semiconductor/metal junction devices. The chemical structure of the molecule/GaAs adducts is optimized ab initio and discussed for the first time. A strong binding scheme is found, providing useful insights about the microscopic structure of the molecular layer. A widely used model based on molecular dipole layers is discussed and verified, by computing the dipole moment for the isolated systems and estimating the charge separation in the adducts; moreover the molecular orbitals energies are analyzed and correlated to the experimental measures of the modified surface electron affinity.

1. Introduction

Molecular monolayers adsorbed onto semiconductor (SC) and metal surfaces can finely tune their electrical properties.^{1–3} The performance of electronic and optoelectronic devices involving such modified surfaces can be effectively enhanced by adapting the chemical nature of the adsorbed molecules.^{4–8} The molecular control of the surface properties has been widely investigated in recent years, and an impressive amount of experimental findings has accumulated.^{9–13} In many cases it has been found that the molecular layer affects the solid-state electronic behavior without the need of an actual charge transport across the organic moiety. Rather, the effect is often due to the static interactions between the molecule and the solid nuclear and electronic densities.^{8,14}

Clearly, the use of such surface treatments is very promising for nanoelectronic applications, thanks to the great variety of available molecules and the relative ease to design and synthesize new, specifically tailored species. Polyfunctional molecules are commonly employed, with some groups designed to ensure a strong binding to the surface (e.g., thiols for grafting to gold^{11,15} or other metals, carboxylic acids for semiconductors as TiO₂¹⁶ or GaAs,^{17–21} ene or diene groups for silicon,^{22–23} silanes for oxidized Si,²⁴ etc.) and other groups designed for the specific chemical and physical functions required.²⁵ Among the numerous applications, one can cite molecular sensors for organic and biochemical species,²⁵ modified diodes,^{15,17,18,26} transistors, and other electronic devices,^{27,28} and also dye-sensitized photovoltaic cells,^{16,29} that however imply an electron transfer between the molecular layer and the underlying semiconductor.

Due to the extremely rich choice of functional groups that can be combined on the molecular side, an efficient design of such devices requires a clear understanding of the microscopic interactions between the molecules and the solid substrate. In this field, it is highly desirable that the synthesis and the characterization of these hybrid systems be assisted by a suitable

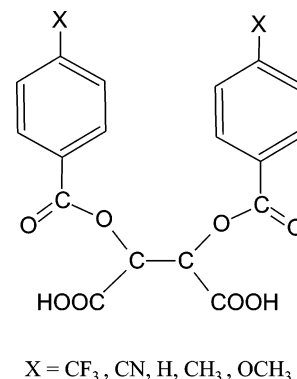


Figure 1. Lewis structure of the substituted dicarboxylic acid.

theoretical modeling, using high level ab initio techniques (necessary as long as one is interested in the details of the electronic distribution at the interface). The most efficient approaches are rooted in density functional theory (DFT), which is being extensively used both for the study of molecular systems (also of quite large dimensions,^{30–32} thanks to the most recent algorithms) and for the modeling of periodic systems as bulk solid materials or surfaces.^{33–36}

In this paper we model a GaAs (001) surface covered by a monolayer of substituted dicarboxylic acid (dC–X, with X = CF₃, CN, H, CH₃, OCH₃ indicating the varying substituent, see Figure 1). This system has been widely studied and its electrical behavior in SC/molecule/metal junctions is well-characterized.^{14,17,37–38} It is seen that the current/potential curves for such devices are strongly dependent on the acid substituent,³⁹ the electron-withdrawing groups inducing higher currents at the same potential. Another measured quantity is the contact potential difference between the modified semiconductor surface and a metal surface⁴⁰ (in this measure the two parts are connected electrically, but not spatially). Even in this case, the potential difference depends on the organic substituent markedly.

The presence of the molecular layer modifies the GaAs surface work function, which in turn affects the device proper-

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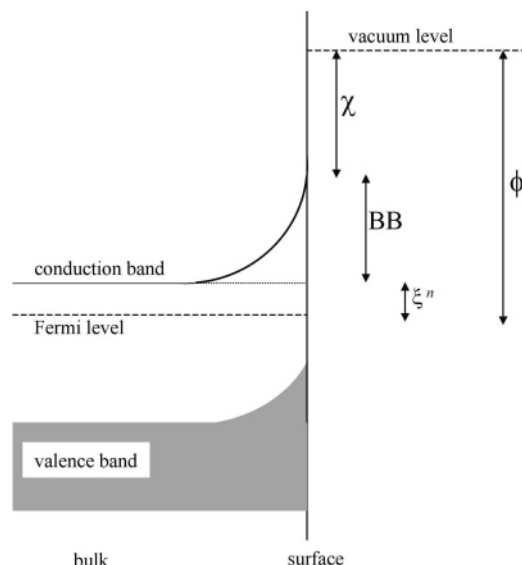


Figure 2. Contributions to the SC work function.

ties.⁴¹ In a n-type semiconductor, the work function is defined as $\phi = \chi + BB + \xi^n$, where χ is the electron affinity (EA), that is the difference between the energy of a free electron very close to the surface (the “vacuum level”) and the bottom of the SC conduction band, BB (band bending) is the difference between the band energy on the surface and in the bulk (due to localized electronic states on the surface), and ξ^n is the difference between the SC Fermi level and the bottom of the conduction band; these quantities are illustrated in Figure 2. Note that all the energies are taken in absolute values. When a molecular layer is adsorbed on the surface, both the EA and the band bending are modified. When the contact potential difference is measured under strong illumination,⁶ however, the BB effect can be eliminated, isolating the EA change ($\Delta\chi$).

The $\Delta\chi$ observed upon adsorption of dC–X monolayers on a GaAs surface are often interpreted with a simple model,^{3,40} in which the molecules are assimilated to dipole moments (forming an average angle θ with the normal to the surface). A dipole layer is always present on free surfaces. For instance, in n-type SC the electronic charge concentrates in the surface states, leaving the positive countercharge in the underlying solid (see Figure 3a). The adsorbed molecular layer can be seen as an additional dipole layer (Figure 3b). When the dipoles are oriented with the positive head toward the surface, the electron transfer from the vacuum state to the SC conduction band is favored, that is, $\Delta\chi > 0$.

If μ is the absolute value of the dipole associated to one dC–X molecule, the expected EA change is (in atomic units)

$$\Delta\chi = \frac{N\mu \cos(\theta)}{\epsilon} \quad (1)$$

where N is the surface density of adsorbed molecules and ϵ is the dielectric constant of the layer. In this model, the relevant microscopic quantities are the molecular dipole and the average orientation on the surface (of course, as far as trends in homogeneous series are searched for, one can assume that the orientation is constant to a good extent). Indeed, previous theoretical studies concentrated on the calculation of dipole moments, mostly with semiempirical techniques,⁴⁰ even if some ab initio treatments¹⁸ have appeared also. For the dC–X series, good correlations were found between the computed dipoles and the observed $\Delta\chi$ values. In these works, however, isolated molecules were considered, assuming that the computed dipoles

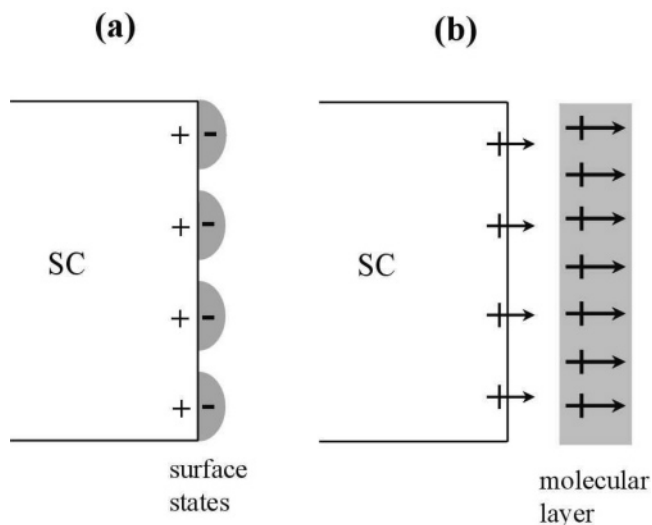


Figure 3. Dipole layer due to surface states (a) and to the adsorbed molecular layer (b).

could be transferred to the monolayer. In the following, we will examine to what extent this assumption is justified and, more generally, whether the dipole model is suitable to describe the experimental trends. We will also concentrate on the structure of the dC–X/GaAs adducts (using a cluster model for the semiconductor), since the details of the chemical bonding at the molecule/surface interface are of great interest per se and can provide useful insights about the nanoscale structure of the monolayer. Moreover, the molecular orbitals before and after the adsorption process will be considered, since this is the quantity more directly related to the electron affinity from the chemical point of view. On the other hand, we will not consider the monolayer effects on the band bending, which is also important in actual devices and could be affected by the chemical bonding too, for the reasons briefly presented in the following. However, this issue deserves to be considered in further work.

2. Methods

Density functional theory (DFT), as implemented in the Gaussian03 package,⁴² has been used for all the calculations, with the PBE1PBE (also called PBE0) density functional. This is a hybrid functional (thus containing a part of the exact exchange interaction), based on the Perdew, Burke, and Ernzerhof functional (PBE)⁴³ and modified as reported in ref 44, that has proved to be very reliable for the calculation of organic molecule electronic properties.⁴⁵

In all electron calculations, the Pople basis set 6-31G⁴⁶ has been employed, supplemented when necessary by extra polarization functions on hydrogen and heavy atoms⁴⁷ and by diffuse functions on heavy atoms⁴⁸ (the resulting set is indicated as usual as 6-31+G(d,p)). On some atoms of the GaAs cluster, the LANL2DZ set of pseudopotentials and basis⁴⁹ has been used.

The cluster geometry was obtained as follows: First, seven layers (with Ga atoms on top and bottom) were extracted from the GaAs bulk crystallographic structure forming a (001) surface, and a Ga₂₀As₁₆ cluster was cut out; four oxygens were added above the top layer, in bridging positions, and all the valences of the underlying layers were filled by hydrogens (see section 4 below). Then the geometry was optimized at the DFT level, with the PBE1PBE functional and a mixed basis set: LANL2DZ pseudopotentials and basis on the third row atoms, 6-31G on oxygens and hydrogens. The positions of all the heavy atoms

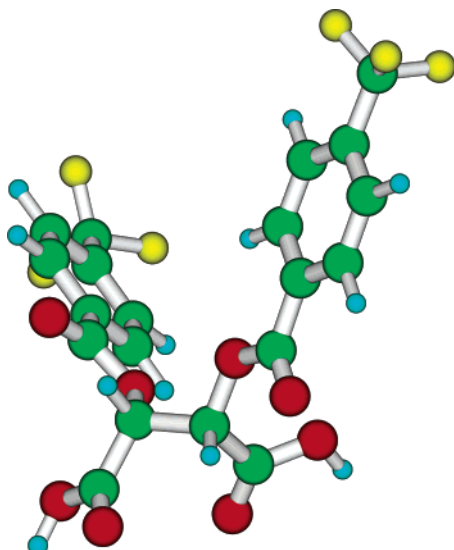


Figure 4. dC-CF₃ structure optimized at the PBE1PBE/6-31G(d,p) level.

TABLE 1: Substituted Dicarboxylic Acid Molecular Dipoles (norm and “vertical” component, see text), Computed at the PBE1PBE/6-31+G(d,p) Level, along with the Measured Changes in Electron Affinity of Covered GaAs Surfaces

substituent	dipole norm (D)	direction ^a	dipole vertical component (D)	$\Delta\chi^{40}$ (eV)
CH ₃	6.23	—	-5.03	-0.25
OCH ₃	6.11	—	-5.6	-0.24
H	5.24	—	-4.43	-0.23
CN	3.19	+	2.99	0.16
CF ₃	1.52	+	0.23	0.14

^a Conventionally positive if the positive head points toward the acid group.

in the first five layers (counting from bottom) were frozen in their bulk values, so that only the geometry of the two top As and Ga layers and of O and H atoms was allowed to relax. Recently, a similar approach (DFT calculations on the same cluster) was used to study the electronic properties of the GaAs oxidized surface, finding a good agreement with the results obtained with plane waves on periodic slabs.⁵⁰

Localized charges in the molecule-on-cluster systems were computed according to the Hirshfeld procedure.⁵¹

3. Isolated Molecules

The geometry of the five substituted dicarboxylic acids (dC-X, with X = CF₃, CN, H, CH₃, OCH₃, Figure 1) was optimized at the PBE1PBE/6-31+G(d,p) level. In Figure 4 the resulting structure for dC-CF₃ is shown. The backbone structure is very similar for all the substituents. Clearly, the two arms prefer a screwed arrangement, in which one of the benzene hydrogens interacts with the π system of the other ring, while the carbonyl oxygens in the arms are involved in two (likely loose) H-bonds with the hydrogens linked to the sp³ carbons.

As reported in the Introduction, to understand the changes in the SC surface electron affinity, the organic monolayers are often depicted as a collection of electric dipoles adsorbed on the surface. The electric dipoles of the five molecules were computed with PBE1PBE/6-31G+(d,p), with the results listed in Table 1; the correlation with $\Delta\chi$ is illustrated in Figure 5. Electron-donating substituents, as -H, -CH₃, and -OCH₃, induce a molecular dipole with the negative head pointing toward the acid groups (i.e., the side of the molecule which

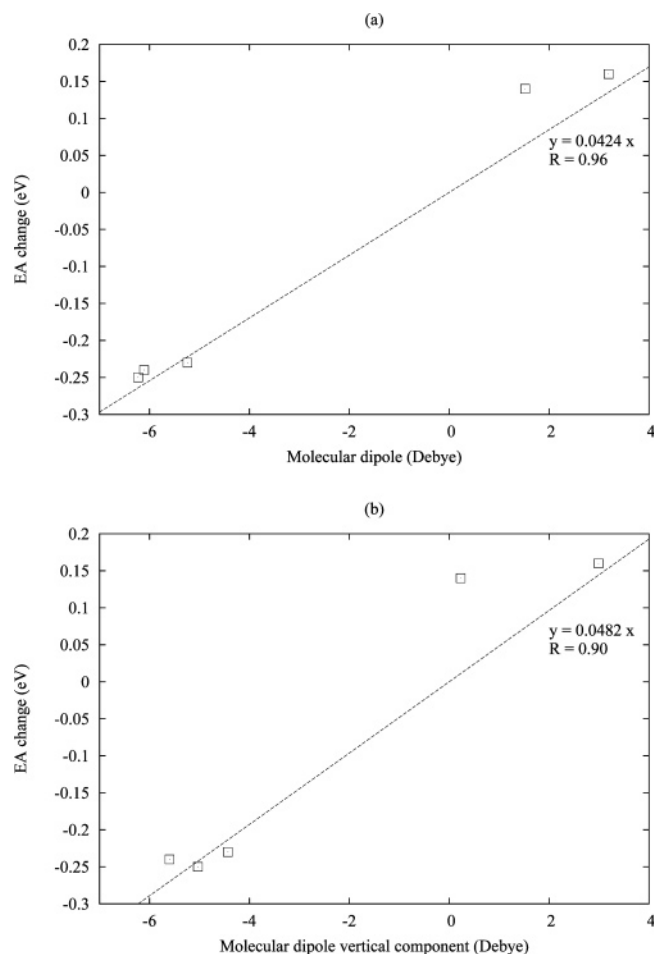


Figure 5. dC-X molecular dipoles vs the observed changes in modified GaAs surface electron affinity: (a) dipole norm; (b) dipole vertical component.

will be used to bind to the surface). As discussed above, this corresponds to a negative dipole layer, which is expected to decrease the surface electron affinity ($\Delta\chi < 0$). The opposite is true for the electron-withdrawing substituents, i.e., -CN and -CF₃.

Of course, the molecular dipole *norm* is not the best descriptor, since the observed effect is due to the normal component with respect to the surface. Assuming that the molecular structure does not change too much after the adsorption, one could expect a better correlation using the dipole “vertical” component, i.e., the projection on the direction perpendicular to the bond between the sp³ carbons (the dicarboxylic acid backbone). As shown in Figure 5, both the norm and the vertical component correlate quite well with the observed $\Delta\chi$ ($R^2 = 0.96$ and 0.90 , respectively), even if the latter is less satisfactory, contrary to what is expected. A possible reason can be the actual orientation assumed by the molecules on the surface, or a strong change in the molecular geometry upon adsorption. This point will be investigated in the next sections.

Ab initio calculations also provide good estimates for the molecular orbital energies (though in single-determinant approaches virtual orbitals are by definition less accurate than occupied orbitals, those lying at low energies are usually considered reliable as well). As mentioned in the Introduction, the molecular layer is seen to affect the SC band bending too ($\Delta BB < 0$, resulting in a work function increase), and this effect can be interpreted as due to the interaction between the first unoccupied molecular orbitals and the surface states. In Table

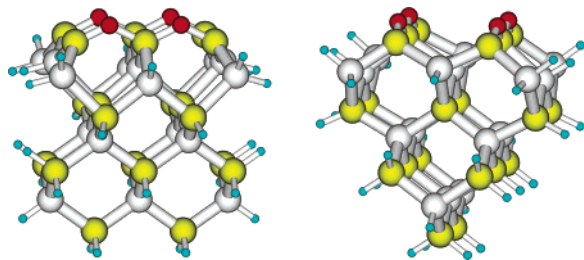


Figure 6. Two views of the oxidized GaAs cluster, optimized as described in the text: top layer of Ga atoms linked to oxygen.

TABLE 2: Substituted Dicarboxylic Acid HOMO and LUMO Energies (eV) and Measured Changes in the Band Bending (eV) of Covered GaAs Surfaces

substituent	HOMO	LUMO	ΔBB^{52}
CH ₃	-7.376	-1.529	n/a
OCH ₃	-6.837	-1.312	0.40
H	-7.686	-1.670	0.29
CN	-8.272	-2.714	0.18
CF ₃	-8.262	-2.310	0.38

2 we report the dC-X HOMO and LUMO (highest occupied and lowest unoccupied molecular orbitals, respectively) energies, computed with PBE1PBE/6-31+G(d,p), along with the ΔBB measured for GaAs surfaces covered by the corresponding monolayers.

The isolated molecule HOMO and LUMO energies bracket the SC Fermi level (approximately -3.8 eV for n-type GaAs). The LUMO energy, in particular, is quite higher than the surface state energies (expected to be close to the Fermi level), and this opposes the idea of a strong molecule/surface interaction. As a matter of fact, no clear trend can be drawn from the data in Table 2, columns 2 and 3. Then, the observed ΔBB should be analyzed in terms of the orbitals formed after the adsorption; however, the cluster model used in this article for GaAs is not the best choice to describe the surface states, and this analysis is deferred to a future work, in which the inorganic layer will be treated with a different approach. In the following we concentrate on $\Delta\chi$, recalling that the two effects can be separated by performing the measures with and without a strong illumination of the sample.^{6,40}

4. Oxidized GaAs Cluster

To investigate the effects of the molecule–semiconductor interactions, we modeled the GaAs oxidized (001) surface with a Ga₂₀As₁₆O₄H₃₂ cluster. The optimized structure, obtained as previously described (see section 2), is illustrated in Figure 6.

The top layer comprises six Ga atoms with four bridging oxygens, leaving four unsaturated orbitals (often referred to as “dangling bonds” in surface science) on the most external Ga atoms, while the underlying layers contain tetraordinated atoms only. The surface unsaturation is a well-known feature of many semiconductors, even after the more or less extended reconstructions which occur when the surfaces are prepared.

Scanning tunneling microscopy images of unoxidized GaAs (001) surfaces⁵³ showed planes of Ga atoms covered by couples of As dimers arranged in lines separated by quite deep trenches (see Figure 7 for a schematic picture, and ref 53 for more details). It has been seen that when the surface is oxidized, the most favored reaction is the substitution of As dimer couples by four oxygen atoms, even if other arrangements are possible, like O atoms bound inside the trench, or bridging between two couples.⁵⁴ Anyway, our cluster mimics the most likely situation, i.e., one “island” of four oxygen atoms, slightly higher than

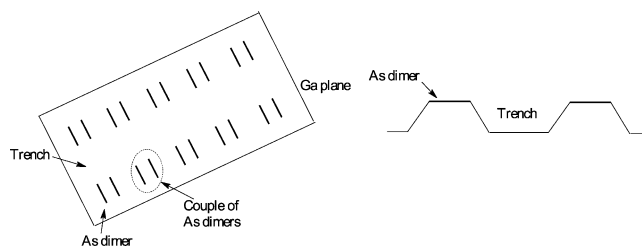


Figure 7. Schematic picture of the unoxidized GaAs (001) surface.

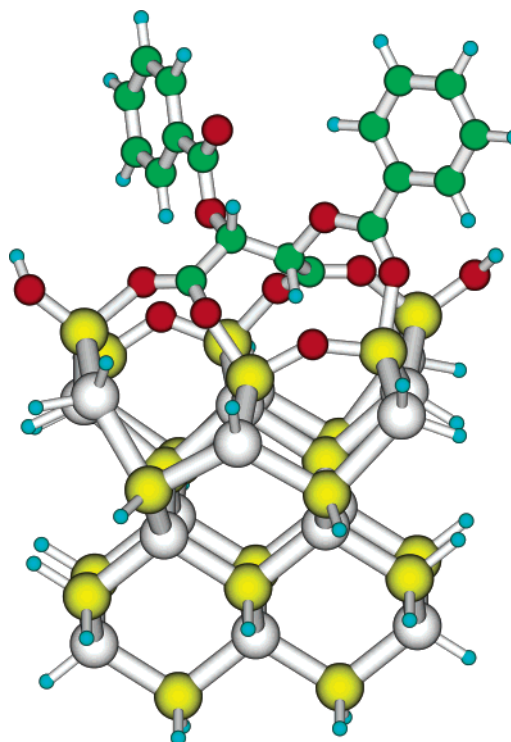


Figure 8. Structure of dC-H adsorbed on the GaAs cluster.

the SC surface, bridging the six underlying Ga atoms: in the ideal fully oxidized surface, such islands substitute all the As dimer couples shown in Figure 7.

5. Molecules Adsorbed on the Cluster

The five substituted dicarboxylic acids were adsorbed on the GaAs cluster previously described, using the acid moieties as binding groups. The geometry of the adducts was optimized with PBE1PBE and the mixed basis set (LANL2DZ on Ga and As, 6-31G on all the other atoms). The structure of the dC-H adduct is shown in Figure 8; the other substituents have a little effect on the geometry. In particular, the position of the arms is similar in all the systems.

We find that the oxide layer on top of the cluster is markedly more basic than the organic oxygens, confirming previous observations. Basically all our optimizations started with the undissociated acids but ended with the acidic hydrogens transferred to the oxide, forming two hydroxylic groups still bound to the surface. The carboxylic oxygens have a strong affinity for the Ga atoms and four Ga–O bonds are formed; moreover, in all the adducts one of the carbonylic oxygens binds to another Ga atom. The structure is further stabilized by an H-bond between one of the benzene hydrogens and the second carbonylic oxygen, which is not bound to the surface. The adduct is very stable (for instance, the ΔH of formation with respect to the separate partners for dC-CF₃/GaAs is -139 kcal/mol at this computational level).

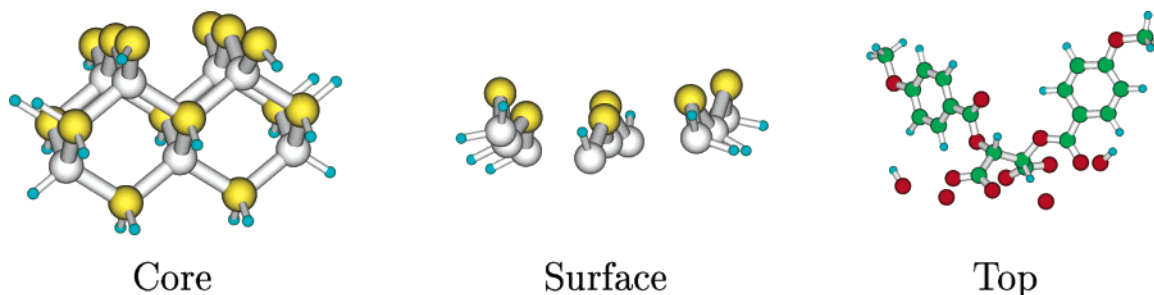


Figure 9. Layers defined for the calculation of localized charges: dC-OCH₃ adduct.

TABLE 3: dC-X Molecular Dipoles (norm and “vertical” component), Computed with PBE1PBE/6-31+G(d,p) at the Same Geometry as in the Adducts, Angles between the Dipole and the Normal to the Surface, and Experimental Changes in the Electron Affinity of Covered GaAs Surfaces

substituent	dipole norm (D)	direction ^a	angle (deg)	dipole vertical component (D)	$\Delta\chi^{40}$ (eV)
CH ₃	4.61	—	38	−2.85	−0.25
OCH ₃	4.90	—	52	−3.86	−0.24
H	3.80	—	32	−2.01	−0.23
CN	4.36	+	31	3.70	0.16
CF ₃	2.95	+	45	2.08	0.14

^a Conventionally positive if the positive head points toward the acid group.

A two-site adsorption mechanism had already been postulated for dC-X's on GaAs^{19,56} with both the acid terminations involved in bridging coordination bonds (more experimental evidence exists on monocarboxylic acids, like benzoic acid, which forms a similar bridging bond between a single couple of Ga atoms).^{12a} As an alternative to the present structure, the two acid moieties could bind to different “islands” of oxidized Ga along the same line or cross the trench between parallel lines (see Figure 7 and the discussion in section 4). However, the adduct structure illustrated in Figure 8 is most likely (though there is no direct experimental evidence), since the distance between the dC-X acid groups in the free molecules is very close to the distance between the two couples of Ga atoms actually involved in the bonding. On the contrary, the distance between successive islands and the distance across the trench are too large for such an effective multiple bond.

The geometry of the organic moiety is quite distorted in the adduct, especially because the two arms are closer than those in the free molecules, and one of them is rotated in order to form the intramolecular H-bond. Due to this geometry distortion and to the electronic interactions with the cluster atoms, it is questionable whether the dipole moments computed for the free molecules can be used to explain the adduct properties. The distortion effects can be evaluated by recomputing the dC-X dipoles at the same geometry as in the adducts (with the two acidic hydrogens bound to the corresponding carboxylic oxygens). The results are collected in Table 3. We report the dipole norms, along with the angle between the dipoles and the direction perpendicular to the plane of the carboxylic oxygens (approximately parallel to the cluster “surface”), corresponding to the angle θ in eq. 1. Also reported is the dipole “vertical” component, i.e., the projection onto this perpendicular direction.

By comparing the values in Table 3 to their counterparts for the isolated molecules (Table 1), one can see that the dipoles are quite affected by the distortion, but the signs and the trend agree. Actually, the correlation with the observed $\Delta E A$ ($R^2 = 0.97$ for the norms and 0.89 for the vertical components) is very similar to that obtained with the optimized structures ($R^2 = 0.96$ and 0.90, respectively, see above).

TABLE 4: Layer Charges (a.u.) Computed at the PBE1PBE/6-31G

system	top layer charge ^a	surface layer charge	core layer charge
free cluster	−1.70	2.71	−1.01
dC-CH ₃	−1.27 (0.14)	2.39	−1.11
dC-OCH ₃	−1.26 (0.16)	2.38	−1.12
dC-H	−1.28 (0.13)	2.40	−1.12
dC-CN	−1.33 (0.08)	2.40	−1.06
dC-CF ₃	−1.32 (0.09)	2.41	−1.09

^a Oxide layer (4 O's) in the free cluster, oxide layer + molecule in the adducts. The charge on the molecular arms is given in parentheses.

To include also the electronic effects, we have to compute the “molecular” dipole once the acid is adsorbed on the cluster. Of course there is no unique definition for this quantity; nevertheless a reasonable approximation can be obtained by means of some localization techniques. We used localized atomic charges according to Hirshfeld's scheme, which is more reliable than the simple Mulliken approach but still much faster than Bader analysis. Hirshfeld atomic charges were computed at the PBE1PBE/6-31G(d,p) level (thus using the polarized all-electron basis set for all the atoms), for the oxidized GaAs cluster and for the five adducts, at the geometries previously optimized. Different layers were defined: the “core”, formed by the Ga and As atoms of the first five layers, counting from bottom; the “surface”, formed by the two top layers of Ga and As; and the “top”, containing the four oxygen atoms in the bare cluster and the oxygens plus the adsorbed molecule in each adduct. In all cases, the hydrogens were included in the same layer as the heavy atoms they are bonded to. In each layer the “center of charge” was defined as the average of the atomic positions in the layer weighted by the corresponding charges. The layers are depicted for the dC-OCH₃ adduct in Figure 9, and the atomic charges summed up in each layer are listed in Table 4.

In all cases there is a clear charge separation. The surface layer provides electronic charge to the top and to the core, resulting positive. In the free cluster the surface is slightly more positive than in the presence of the adsorbed molecules. The dC-X's transfer an amount of electronic charge to the oxide layer, and the oxygens are in general less eager to draw charge from the underlying Ga atoms. As a consequence, the molecular arms become slightly positive, even if the effect is understandably smaller for electron-withdrawing X. This is an indication that the use of the gas-phase molecular dipoles could be misleading. As a matter of fact, if a “molecular” dipole could be exactly defined in the adducts, it would have a negative sign (i.e., with the positive head far from the binding site) in all the cases, though the measured $\Delta\chi$ has a different sign for some substituents (see Table 1).

On the other hand, the data collected in Table 4 seem to indicate that the charge double layer is smaller when the surface

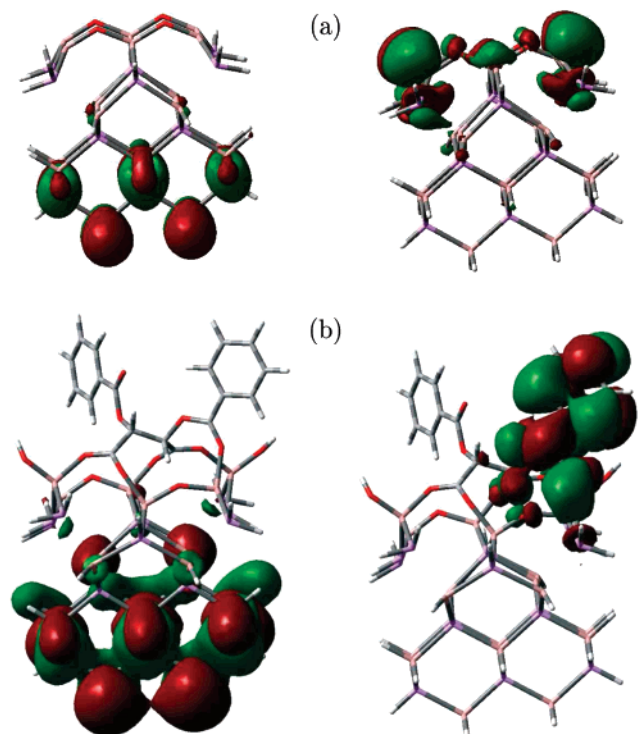


Figure 10. HOMO and LUMO orbitals for (a) the bare cluster and (b) the dC-H/GaAs adduct.

is covered by dC-X molecules than in the simple oxidized surface. We can try to express this physical quantity in terms of surface dipoles by concentrating the oxygen and dC-X charge in the top layer charge center and placing the same charge with the opposite sign in the surface layer charge center (i.e., concentrating here all the surface and core charge, leaving the “bulk” of the semiconductor neutral). In this model, the surface dipole is 2.93 D in the free (oxidized) cluster, and 5.87, 5.95, 5.66, 6.01, 6.08 D with adsorbed molecules (the order of the substituents is the same as in Table 4, first column, and the dipole sign is positive according to the convention explained in section 3). If we consider the free oxidized cluster as a model for the bare semiconductor surface (without molecules attached), the dipoles reported above do not correlate at all with $\Delta\chi$, since

they are systematically larger than 2.93 D, while the measured electron affinity change has a different sign according to the substituent. Ignoring the free cluster result, we observe that the adduct dipoles do depend on the substituent in the correct way ($-\text{CN}$ and $-\text{CF}_3$ more positive, corresponding to larger EA); however the correlation with the experimental $\Delta\chi$ is very poor ($R^2 = 0.50$).

Actually, the adduct dipoles listed above are larger than the free cluster dipole only because the center of charge is further from the surface; placing the top charge in the same point as in the free cluster, the dipoles with attached dC-X become 2.27, 2.30, 2.20, 2.19, 2.17 D (lower than the free cluster dipole, as expected from Table 4 data). Anyway the correlation with $\Delta\chi$ remains pretty poor ($R^2 = 0.65$).

To model the molecular effects from a more chemical viewpoint, we computed the LUMO energies for the free oxidized cluster and for the adducts, since this is the quantity most directly related to the electron affinity at this theoretical level. It is well-known that the absolute value of the Kohn-Sham orbital energies can be quantitatively unreliable (particularly for virtual orbitals); nevertheless we believe that the energy *trend* in such a homogeneous series of compounds can be safely used to correlate the observed $\Delta\chi$ values. It is worth noting that in the free cluster the LUMO is located on the oxide layer, while in all the adducts the LUMO and most low-lying unoccupied orbitals concentrate on the molecular moiety, so that their energy is affected by the chemical nature of the organic substituents significantly. On the contrary, the highest occupied orbital always lies in the inorganic moiety; see Figure 10 for an illustration of the HOMO and LUMO orbitals in the bare cluster and in the dC-H adduct.

The LUMO energies are reported in Figure 11, along with the corresponding HOMO energies, for comparison. As expected, the HOMO levels are much less dependent on the organic substituents, and in all the adducts their energies are slightly less negative than that in the bare cluster. The LUMO energies, on the other hand, depend on the adsorbed molecule markedly, and they show the expected trend with the substituent electronegativity, being more negative with electron-withdrawing substituents which leave the rest of the molecule less rich in electron density and thus more eager to accept the incoming charge. As illustrated in Figure 12, the correlation of the

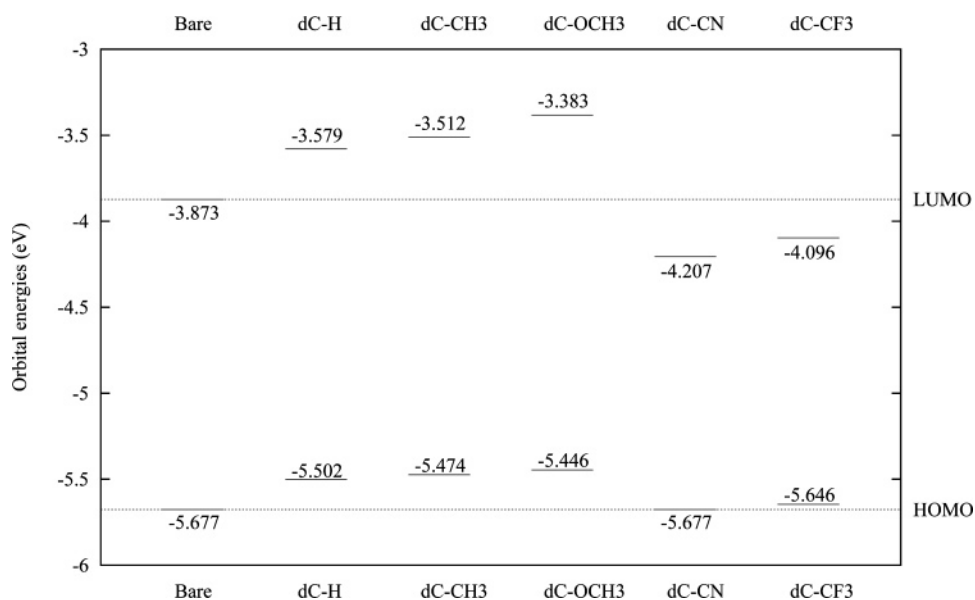


Figure 11. HOMO and LUMO levels for the bare oxidized GaAs cluster and the adducts.

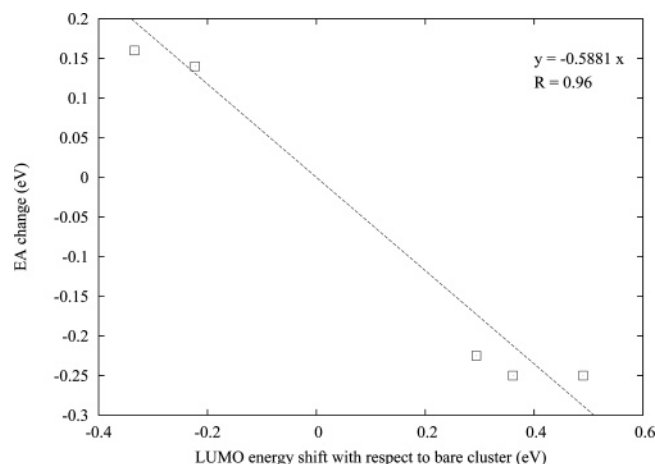


Figure 12. Observed changes in modified GaAs surface electron affinity vs the GaAs/dC–X adduct LUMO energy (referred to the bare cluster LUMO).

measured $\Delta\chi$ with the adduct LUMO energies (referred to the bare cluster LUMO level) is quite good ($R^2 = 0.96$)

6. Conclusions

We have studied at the DFT level the adducts of substituted dicarboxylic acids (dC–X) on GaAs (001) surface, with the aim to clarify the microscopic interactions responsible for the electric behavior of the modified surfaces. In particular, we concentrate on the measured change in electron affinity, as defined in the Introduction, due to the molecule adsorption; in all the calculations the semiconductor was modeled as a $\text{Ga}_{20}\text{As}_{16}$ cluster, suitably saturated with hydrogens and covered by an oxide layer.

The structure of the dC–X/GaAs adducts was optimized for the first time at the ab initio level. The acidic hydrogens are transferred to the inorganic oxide layer, and a strong molecule/cluster binding is found, involving five organic oxygens and Ga atoms. The dC–X geometry is strongly distorted upon adsorption, and the molecule body forms an angle of 30–50°, according to the substituent, with the normal to the surface.

A good correlation is found between the electric dipole moments of isolated dC–X and the measured $\Delta\chi$ of the modified surfaces, confirming previous results obtained at lower computational levels; however, the correlation is slightly worse considering the normal component of the dipole, contrary to what expected on the basis of the simple “dipole layer” model presented in the Introduction. Moreover, due to the geometry distortion experienced by the adsorbed molecules, it seems unlikely that the isolated system dipoles are directly related to the adduct properties. After the adsorption, it is possible to model the electric double layer at the molecule/semiconductor interface by means of localization techniques (in our case, Hirshfeld’s charges were used). The results are not completely satisfactory, since in all the adducts the double layer is found to be smaller than in the free (oxidized) surface, while the observed $\Delta\chi$ has different signs for different substituents. However, the relative trend of dC–X/GaAs surface charge separation correlates quite well with the electron affinity changes.

A better correlation is found by computing the molecular orbital energies of the adducts. The LUMO orbital concentrates on the oxide layer in the free cluster, and on the molecular arms in the adducts (while the HOMO is always located in the cluster core), and the relative energies follow the same trend of the experimental EAs, with a linear coefficient $R^2 = 0.96$. From this viewpoint, the good trend of isolated dipole moments with

$\Delta\chi$ can be better explained with the strong correlation between the dipole and the LUMO energy, being these quantities are both strongly dependent on the electronegativity of the acid substituents.

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