

Probing Organic Layers on the TiO₂(110) Surface

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In this work, we use first principles simulations to provide features of the dynamic scanning force microscopy imaging of adsorbed organic layers on insulating surfaces. We consider monolayers of formic (HCOOH) and acetic (CH₃COOH) acid and a mixed layer of acetic and trifluoroacetic acids (CF₃COOH) on the TiO₂(110) surface and study their interaction with a silicon dangling bond tip. The results demonstrate that the silicon tip interacts more strongly with the substrate and the COO⁻ group than the adsorbed acid headgroups, and, therefore, molecules would appear dark in images. The pattern of contrast and apparent height of molecules is determined by the repulsion between the tip and the molecular headgroups and by significant deformation of the monolayer and individual molecules. The height of the molecule on the surface and the size of the headgroup play a large role in determining access of the tip to the substrate and, hence, the contrast in images. Direct imaging of the molecules themselves could be obtained by providing a functionalized tip with attraction to the molecular headgroups, for example, a positive potential tip.

I. Introduction

In recent years dynamic scanning force microscopy (D-SFM) has demonstrated its ability to provide atomic resolution on a wide variety of semiconducting and insulating surfaces,^{1–3} including breakthrough results in the application-rich area of oxide surfaces.^{4,5} The focus of D-SFM research has diversified, with great attention now being placed on the study and manipulation of adsorbed species on surfaces.^{6–8} D-SFM offers the potential of atomic resolution imaging and manipulation of any molecule/surface combination, unlike the more limited (but better developed) scanning tunneling microscopy (STM). To develop D-SFM in this direction we require a combination of great efforts experimentally and theoretical understanding of the interactions involved. In this work, we use first principles simulations to provide features of the D-SFM tip–surface interaction characteristic to studies of adsorbed organic layers on insulating surfaces. This is also important for understanding the properties of functionalized organic layers on oxide surfaces, an issue of high current interest in many biological applications and corrosion studies.

One of the earliest studies of adsorption in D-SFM was on the TiO₂(110) surface, where a combined STM/D-SFM investigation of a formate (HCOOH) monolayer on TiO₂⁹ provided one of the first nontrivial interpretations of atomically resolved images. By comparing images from both techniques they were able to identify the source of contrast in images of the clean surface. This prompted an extensive D-SFM study^{10–15} of both acetate (CH₃COOH) and trifluoroacetate (CF₃COOH, referred to as 3F-acetate) layers on the surface. This remains the only fully systematic study of adsorption in atomically resolved D-SFM and is also an important general study of imaging organic layers with this emerging technique. Hence, we use these three systems adsorbed on the TiO₂(110) surface as model systems for this study.

The importance of the titanium dioxide (TiO₂) surface in a wide variety of applications, from photocatalysis to biomedical implants, has led to a considerable research effort to understand its properties. The basic physical and electronic structure of the most stable (110) surface has been well-studied both experimentally and theoretically,¹⁶ and now many investigations focus on defected surfaces, especially oxygen vacancies,^{17–19} adsorption,^{20–23} or even adsorption onto defected surfaces.^{24–26}

As a result of their particular relevance to catalysis, many studies have investigated the properties of adsorbed carboxylic (RCOOH) acid layers on the TiO₂(110) surface. The simplest member of this acid group, formate, has been studied extensively^{27–30} and undergoes a dissociative reaction upon adsorption into a carboxylate ion and a proton (RCOOH → RCOO⁻ + H⁺). Some experimental^{31,32} studies on acetate adsorption have also been performed, and the results suggest that the molecule also dissociates at the surface. Recent theoretical work supports this for both acetate and 3F-acetate.³³

In this paper we have studied the interaction of a dangling bond silicon tip and full monolayers of formic and acetic acid and a mixed monolayer of acetic and 3F-acetic acid using first principles methods. The outline of the paper is as follows: in section II we discuss the methods used in the calculations; then in section III we describe the setup of the tip and surfaces; in section IV the results of the calculations are explained and analyzed for each of the systems studied; and then finally in section IV we discuss the implications of the results and compare them to the experiments.

II. Methods

All calculations were performed using the linear combination of atomic orbitals basis SIESTA code,^{34,35} which implements density functional theory in a manner so as to achieve linear scaling in the construction of the Hamiltonian and overlap matrices. Solution of the self-consistent problem can also be performed with linear scaling for insulators, though here full diagonalization is employed so that the electronic structure of

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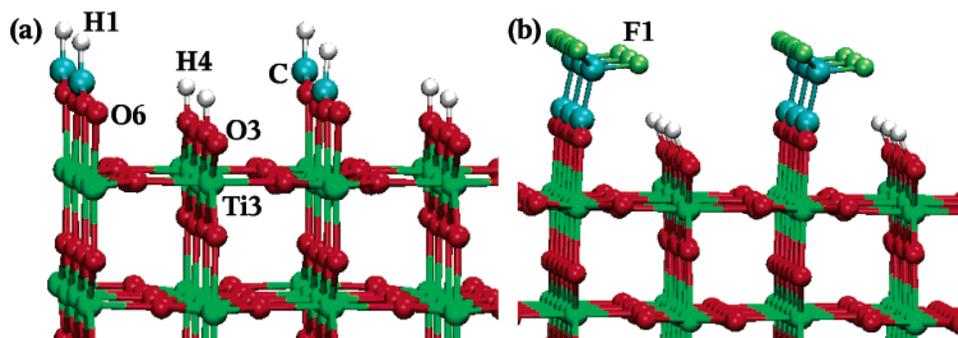


Figure 1. Calculated structures of monolayers of (a) formate and (b) trifluoroacetate adsorbed on the TiO₂(110) surface with key sites labeled.

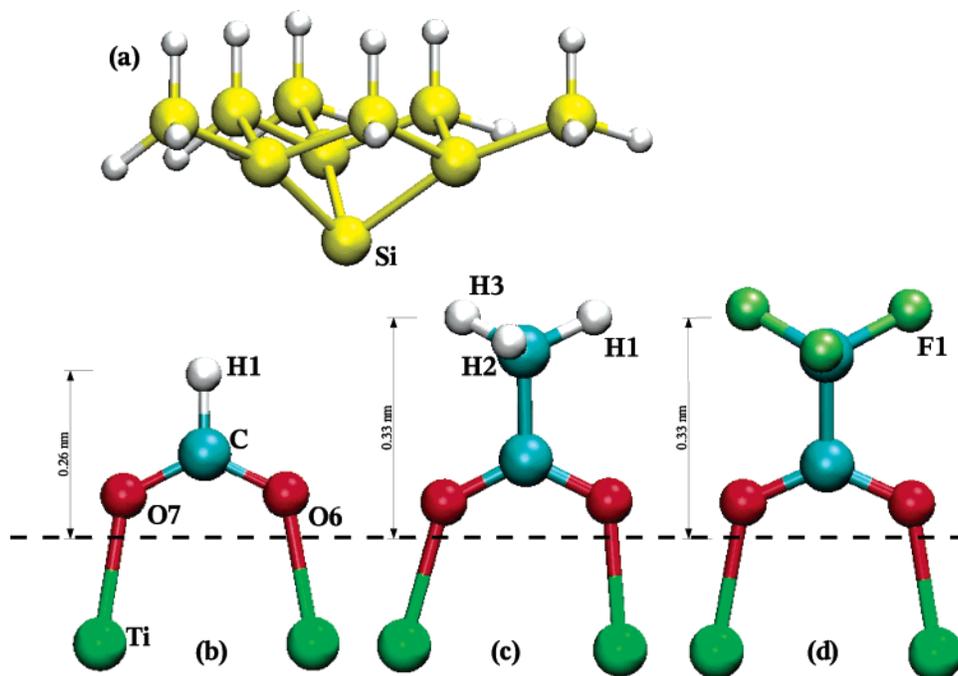


Figure 2. Schematic figure showing the structure of (a) the silicon tip and the adsorbed structure of the (b) formate, (c) acetate, and (d) 3F-acetate molecules on the TiO₂(110) surface. The dashed line shows the height of the bridging oxygen row as a reference for the heights of the molecules.

the surfaces can be studied in detail. The generalized gradient approximation has been utilized in all calculations, based on the specific functional of Perdew, Burke, and Ernzerhof.³⁶ This type of functional has been shown previously to be well-suited to the adsorption of molecules on surfaces,^{37,38} and as such provides a good model for the tip–surface interaction. Core electrons are represented by norm-conserving pseudopotentials of the form proposed by Troullier-Martins,³⁵ and we use the partial core correction scheme of Louie et al.³⁹ All calculations were spin-polarized and implemented a Dirac scalar relativistic correction. The pseudopotential for the titanium atom was generated in the electron configuration [Ar]4s²3d², oxygen in [1s²]2s²2p⁴, hydrogen in 1s¹, carbon in [1s²]2s²2p², and fluorine in [1s²]2s²2p⁵, where square brackets denote the core electron configurations. Various basis set configurations were tested, and a good compromise between accuracy and efficiency was found using double ζ with polarization for Ti, H, C, and F and using triple ζ with polarization for O. All relevant properties of the systems calculated were converged with respect to k points, mesh cutoff, and orbital cutoffs (i.e., energy shift).³⁵ All forces on atoms were relaxed to less than 0.03 nN, providing a displacement accuracy of about 0.001 nm.

The method has been shown previously to provide a good model of the TiO₂ surface¹⁹ and also to provide good agreement

with the experimental properties of the molecules we are considering.³³

III. System Setup

A. Surface. From previous results, the basic structure of the adsorbed layer for each acid on the TiO₂(110) surface is well-known. The acid dissociates, with the proton bonding to a bridging oxygen and the two oxygens of the carboxylate ion bonding to two titanium ions. Figure 1 gives the structure for formate (a) and 3F-acetate (b), and acetate can be considered as having the same structure as 3F-acetate if the fluorine atoms are replaced by hydrogen. The only difference evident in the structures of the three acids is the smaller size of the terminating H atom in formate compared to the CH₃ and CF₃ groups in the acetates. The H atom is at a height of 0.255 nm above the surface plane (defined as the height of bridging oxygens, see Figure 2b–d), compared to 0.326 nm for CH₃ and 0.334 nm for CF₃. The spatial size of the CX₃ groups is also larger, and this results in stronger interaction between the X species and the surface and a tilting of the molecule from vertical (see Figure 1b).

To avoid spurious interactions between images of the tip in the periodic model, we use a (2 × 2) surface cell containing four dissociated molecules to represent the monolayer. A large

vacuum gap prevents any interaction between images in the z direction. The magnitude of this gap depends on the system, but in each case it is large enough so that SIESTA reports no interaction between slabs. For the TiO_2 surface itself, we use a depth of nine atomic layers, with the lower three frozen to represent the bulk. This has been shown previously to well reproduce the measured properties of the surface.¹⁹ In the case of 3F-acetate, to reproduce the experimental setup,¹⁰ we actually use a mixed layer containing three 3F-acetate molecules and a single acetate molecule when calculating the tip–surface interaction. In practice, this makes little difference to forces over a given molecule, for example; the forces over an acetate molecule in the acetate monolayer are very similar to those of an acetate molecule in the mixed monolayer.

B. Tip. The nature of the tip is always a crucial question in understanding D-SFM experiments, because the contrast pattern has been shown to be very sensitive to its atomic structure.³ In general, the tips are microfabricated from silicon, but contamination from the ambient or the surface itself is very likely unless special preparation methods are applied. Previous studies of plain surfaces³ have attempted to use several different tip models to provide a more complete picture of the tip–surface interaction, but here we apply a somewhat different methodology. Because D-SFM experiments of acetate layers on TiO_2 claim a clean silicon tip due to sputtering,¹⁰ we choose silicon as our primary tip material. Recent advances in the preparation^{40,41} and theoretical understanding^{42,43} of silicon tips encourage their general use in D-SFM. As a model of a clean silicon tip, we use a 10 atom silicon cluster with its base terminated by hydrogen.⁴⁴ The interaction of this tip with polar surfaces has three main components due to (i) a negative permanent dipole moment in the direction perpendicular to the surface; (ii) dipole moments induced in the tip due to polarization by the surface; and (iii) the formation of covalent bonds between the dangling bond from the apex Si atom and surface atoms (see Figure 2a). This is a common model of a silicon tip, which has been shown to give good quantitative agreement with experimental forces measured on a silicon surface.⁴⁵ The lower four silicon atoms are allowed to relax freely, but all others are frozen to represent the bulk part of the tip.

IV. Tip–Surface Interaction

To study the tip–surface interaction we consider the force exerted on the silicon tip above various atoms in the surface. In this discussion the tip–surface distance is defined with respect to the highest atom in the undistorted system: H1 for formate and acetate and F1 for 3F-acetate (see Figure 2). This means that the forces over the molecules have a consistent definition and can be easily compared. However, this also means that the tip is 0.07 nm closer to the TiO_2 surface in curves over formate. Figure 3a shows an overhead view of the structure of the acetate layer on the surface, with different atomic sites labeled. For the case of 3F-acetate the structure is very similar, only with H1–H3 replaced by F1–F3. However, in the case of formate, only H1 is present and it lies directly above the C; hence, C is not present in the formate force curves and O5–7 becomes accessible. Note that, although the curve above Ti3 approaches a height of 0, the tip is between molecules and is actually over 0.4 nm from the titanium ion.

A. Formate. Figure 3b shows the tip–surface force over seven atomic sites in the formate layer on the surface. Although there is a reasonable spread of forces, they can be effectively separated into two groups. Over the formate molecule itself, H1, and in close proximity, O5–7, we see either repulsion or

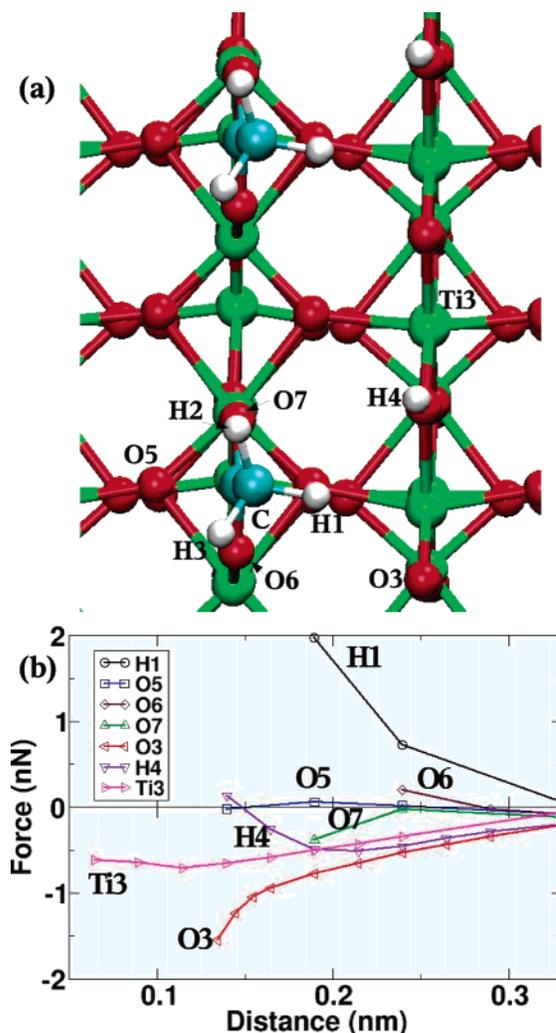


Figure 3. (a) Overhead view of the structure of acetate adsorbed on TiO_2 . (b) Forces between the silicon tip and a formate layer.

very weak attraction. This is an important result, which shows that the inert molecule does not bond with the silicon dangling bond tip and the interaction is mainly due to the onset of electron–electron repulsion at close approach. In contrast, this tip is very reactive with semiconductor and insulating surfaces.^{43,44,46}

The force curves of the second group correspond to sites between the molecules, along the bridging oxygen row (O3–Ti3–H4). Over the bridging oxygen itself (O3) there is strong attraction, which increases rapidly as the tip approaches. Over the proton (H4) and titanium (Ti3) there is also initially strong attraction, but this weakens below 0.15 nm as the maximum is passed. This maximum force over the bridging oxygen row qualitatively matches the tip–surface interaction for the ideal $\text{TiO}_2(110)$ surface.¹⁹ The interaction induces deformations of both tip and surface, which can be split into two categories: tilting of the molecule and of the OH group (proton attached to bridging oxygen) and displacements of tip and surface atoms. In particular a strong tilt of the molecule is observed when the tip is over the O5 site. It tilts as a whole with respect to the bridging oxygen atoms (see Figure 4a). The tilt can be understood as a result of C–H group repulsion from the Si atom at the tip apex. At a large distance (0.295 nm), the C–H bond is contracted by 0.002 nm due to the presence of the Si dangling bond. As the tip approaches closer to the O5 site, the hydrogen atom of formate (H1) displaces in the direction perpendicular

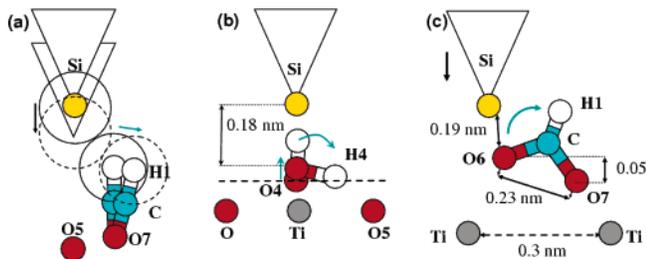


Figure 4. Schematic representation of displacements induced in the TiO₂ surface and adsorbed formate monolayer by the Si tip with dangling bond approaching (a) an O5 site next to the formate molecule; (b) a hydroxylated oxygen (H4); and (c) an O7 site next to the formate molecule. The bold dashed line indicates the level of bridging oxygen atoms as the reference for the height of the molecule.

to the Ti row by 0.001, 0.044, and 0.1 nm, at tip heights of 0.195, 0.145, and 0.105, respectively. The displacement of the C atom is approximately half of the H1 displacement so that the H atom remains in-plane with the COO group. As the tip moves laterally closer to H1 the tilt increases. This does not qualitatively affect the contrast pattern, as the interaction remains repulsive.

Approach to the surface above the O3 ion results in the strongest interaction with the dangling bond silicon tip in the absence of the monolayer.¹⁹ It demonstrates the strongest attractive force also in the presence of a formate monolayer and results in the 0.08 nm displacement of the O3 oxygen in the final point of the force curve at 0.174 nm Si–O distance. The strong attraction at O3 is attributed to the direct interaction of the tip with the bridging-row oxygen, which becomes accessible to the tip as a result of the tilt of the C–H groups of neighboring formate molecules.

Approach to the H4 site is not accompanied by significant deformation until the tip enters into the strong repulsive regime (i.e., force 1.0 nN) at a height of –0.11 nm, and then the O–H bends by about 100° toward the surface (see Figure 4b). The onset of OH bending has a sharp feature in the force–distance curve, which could be observed in experiments. The bending of the OH group exposes the oxygen atom to the silicon dangling bond, and it relaxes 0.052 nm upward so that the Si–O distance becomes 0.186 nm. Such a short distance, close to the Si–O bond length in SiO₂, is indicative of the formation of a bond.

Figure 4c shows another interesting effect as the tip approaches close to the O7 site. Descent of the tip to a height of 0.020 nm results in an 11° rotation of the formate in its plane around the O6 oxygen. Further analysis demonstrates that the Ti–O7 bond is being broken, indicating that in this case the whole molecule could adsorb to the tip. However, at this range the repulsive forces over other sites are very large, and it is unlikely that stable D-SFM operation could be maintained in a real experiment. It does indicate that isolated molecules could be picked up, and a further study of the dynamics of single molecules is presently being performed.

The D-SFM image (see Figure 5) of the formate monolayer in constant frequency shift (CFS) mode was simulated using the force–distance curves obtained on a mesh of 16 points on the surface using typical parameters of the SFM setup and a conventional conversion technique.³ The general contrast pattern for this tip demonstrates dark spots centered over the top site of the formate (H1), which is the site of the strongest repulsion. The brightest spots in the image are over the oxygen atoms of the bridging oxygen row (O3). As a result of the large repulsion over H1, the apex tip atom does not approach the bridging oxygen closer than 0.300 nm in CFS mode, and the oxygen

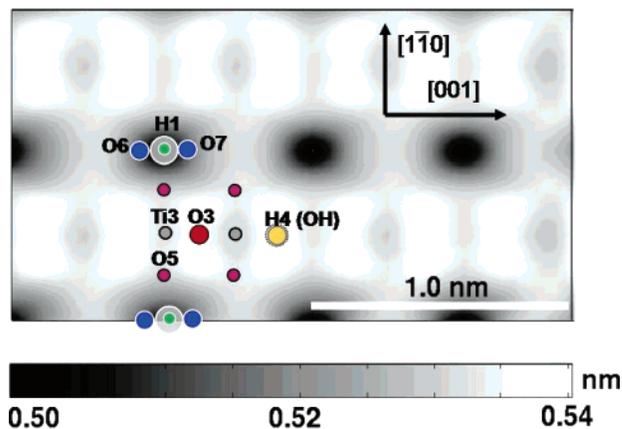


Figure 5. Modeled NC-AFM image of formate monolayer on the TiO₂(110) surface. The tip radius is 50 nm, the normalized frequency shift is 3.5 fN m^{1/2}, the cantilever stiffness is 35 N/m, and the peak-to-peak oscillation amplitude is 10 nm. Colored circles draw correspondence between atomic sites and areas of the image. Red, magenta, yellow, and blue circles represent, correspondingly, bridging, surface, hydroxyl, and formate oxygen atoms.

and hydroxyl sites cannot be distinguished. The same interpretation of the pattern is valid for images taken in constant height mode, except for the relative decrease in intensity over the hydroxyl site at close approach. Interestingly, neither molecules nor the oxygen sites form continuous rows, which results in faint features of 0.2–0.3 nm in diameter. The characteristic force–distance curves detailed in Figure 3b demonstrate that more sites can be resolved and identified if experimental atomically specific force curves are available.^{45,47}

To summarize, there are distinctive features in the force curves of the formate monolayer obtained with a dangling bond Si tip, which govern the contrast formation in the CFS noncontact atomic force microscopy (NC-AFM) image on TiO₂(110). First, the strongest site-dependent interaction is the repulsion over the top formate site, which dominates at all distances. Second, only wide and shallow minima are observed in the force–distance curves despite the strong interactions with surface atoms due to repulsion of the rest of the tip with the soft monolayer. Third, the limits of nondestructive tip approach vary significantly (0.1 nm) across the surface so that the surface is effectively corrugated with respect to the interaction with the Si tip.

B. Acetate. In Figure 6a, we see the two groups of interactions discussed for formate even more clearly defined. The interactions over the acetate molecule (C, H1–H3) are tightly grouped and strongly repulsive below 0.3 nm. The larger size of the CH₃ group compared to that of the H atom of formate means there is no direct access to O5–7 and the interaction is dominated by repulsion from the molecule. Even between the molecules we see that the interaction is very weak, with only a very slight attractive maximum over Ti3. This indicates again that the larger size of the CH₃ group is effectively shielding the surface from the tip, preventing any significant bonding. The Ti3 site lies furthest from the CH₃ group and is least protected, resulting in a maximum in attraction. Note that the magnitude of the force over Ti3 here is an order of magnitude smaller than the force over the same site in the plain surface.¹⁹

The pattern of forces across the surface can also be understood better by considering the displacements of atoms as the tip approaches the surface. When approaching over the molecule, sites C and H1–H3, the general behavior is qualitatively similar: the apex atom of the tip displaces away from the surface and the molecule is “squashed” against the surface. At closest

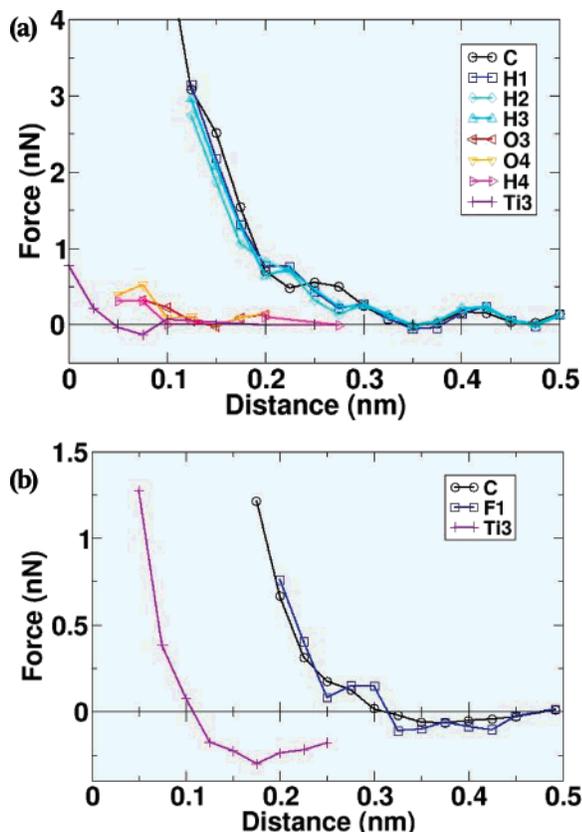


Figure 6. Forces between the silicon tip and (a) an acetate layer and (b) a 3F-acetate layer.

approach over the C site (0.1 nm), the Si apex is displaced upward by 0.06 nm, and the whole C-CH₃ group is pushed down by about 0.01 nm. The Ti and O atoms below the molecule are also pushed down by about half this amount. At 0.125 nm over H1-H3 the overall displacement of the molecule is similar, but now the H directly under the tip displaces much more (0.02–0.03 nm) and the apex Si displaces by only about 0.05; however, there is no significant tilting of the molecule.

The displacements are very different when approaching between the molecules over Ti3, O3, and H4. In these cases, there is almost no relaxation of the tip apex, but there is significant tilting of the molecules upon close approach to make space for the tip. Figure 7a shows how all four molecules bend outward to accommodate the tip as it approaches the central Ti3 site. Over O3, O4, and H4 the less central tip position means that only one of the molecules tilts (see Figure 7b) and the proton displaces toward the tip by about 0.01 nm.

It is worth noting that, in molecular dynamics calculations of the acetate molecule alone,³³ the CH₃ group demonstrates a propensity to rotate around the C-C axis at room temperature. We did not see any evidence of this in the static calculations of the acetate monolayer on TiO₂, nor were any significant rotations induced by the tip. However, we cannot completely exclude its presence at finite temperature.¹⁶

C. 3F-acetate. A similar pattern of interaction is seen in Figure 6b for the 3F-acetate layer. Here we calculate only the interaction over the three most relevant atomic sites: C, F1, and Ti3. Over the molecular sites, the onset of repulsion is very similar to that of acetate, showing that the CF₃ group is equally inert to the silicon tip. However, over Ti3, the interaction is over double that seen for the acetate layer and comparable to that in the formate layer, indicating that the structural size of the CX_n groups perhaps does not give a true indication of their

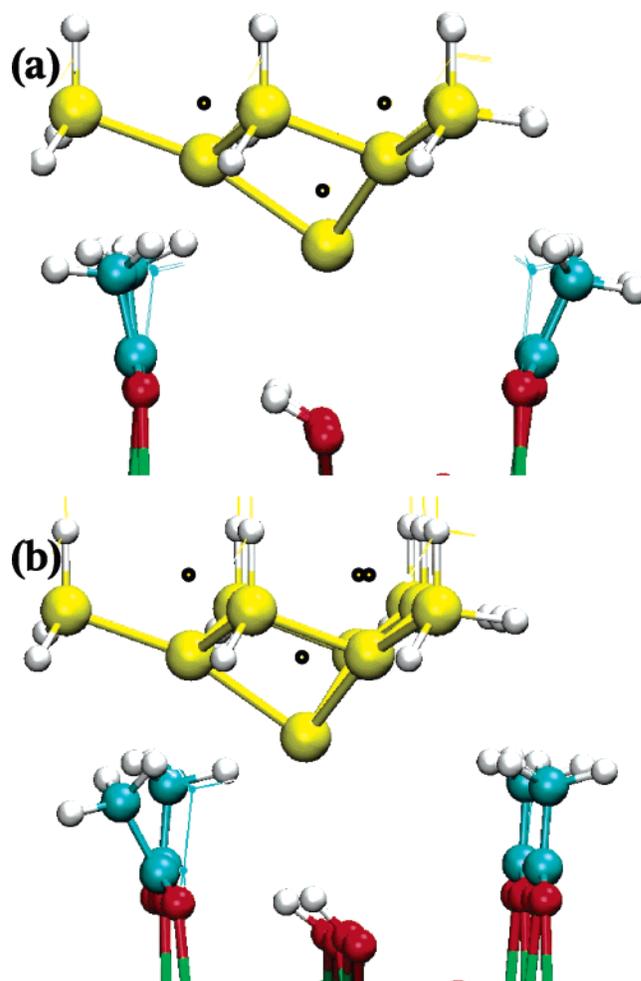


Figure 7. Displacements of atoms as the tip approaches over the acetate monolayer at sites (a) Ti3 and (b) H4. The positions at larger tip-surface distance are shown by dots and lines, whereas the closest approach is shown by atoms and bonds. The distances are 0.1 and 0.0 nm in part a and 0.2 and 0.05 nm in part b.

coverage of the surface: the CF₃ group is actually slightly larger than the CH₃ group.

The displacements for the 3F-acetate monolayer are generally much smaller than for the other systems. At closest approach (0.175 nm) over the C and F1 sites the displacements of the F atoms are less than 0.001 nm (at similar distance above acetate the H displacements under the tip were about 0.01 nm). The only significant displacement of the molecules is that of the C atom, which relaxes downward by 0.004 nm, similar to C in acetate for a similar tip-surface distance. The apex Si atom shows comparable relaxations to acetate, with a displacement upward at closest approach of about 0.05 nm.

The increased rigidity of the C-F bonds is seen even more clearly when the tip approaches between the molecules over Ti3, the CF₃ groups do not displace, and there is no tilting; this results in an increased apex Si displacement of 0.01 nm compared to the same site in the acetate monolayer. Remembering that we have a mixed layer with three CF₃ groups and one CH₃ group, it is worth noting that, when approaching this central site, larger displacements of the CH₃ are seen (as one would expect from the previous section) but no tilting is seen.

D. Electrostatics. These results show that the electrostatic interaction between the polarized tip and the surface molecules plays the dominant role in the tip-surface forces. We can gain insight into this interaction by considering the electrostatic

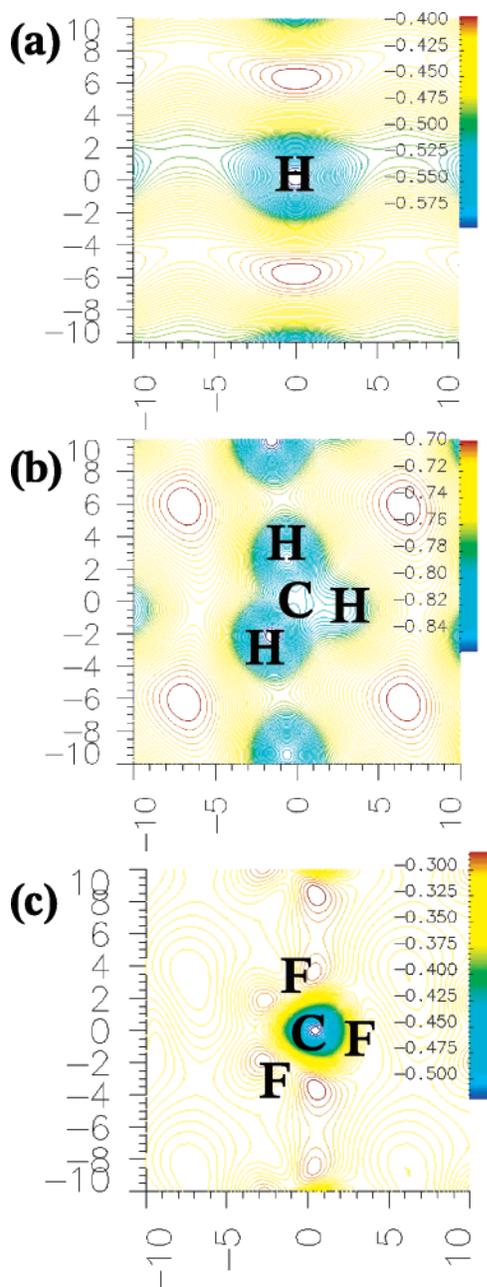


Figure 8. Electrostatic potential plots at 0.2 nm above and parallel to the surface of (a) formate, (b) acetate, and (c) 3F-acetate (eV).

potential of the adsorbed molecules. The definition of electrostatic potential in these calculations is the sum of the Hartree potential and the local pseudopotential. Note that also the absolute value of the potential in these plots is not meaningful, because zero potential is defined at an arbitrary value determined by the local part of the pseudopotentials. In Figure 8 we plot the calculated electrostatic potential of the molecules at 0.2 nm from the highest atom of the adsorbed molecule on the surface. For the formate molecule, Figure 8a shows that the darker area of stronger potential is quite localized around the H1 site. The distribution of the electrostatic potential over CH₃ is different from that in CF₃ (see Figure 8b,c). This difference in electrostatic potential can be understood by considering the nature of the different CX bonds in the molecules on the surface and the Mulliken charges on the atoms. The CX bond in acetate (C^{0.47+}–H^{0.14-}) is actually more ionic than in 3F-acetate (C^{0.15+}–F^{0.06-}). The bond in formate is also of more covalent character (C^{0.05+}–H^{0.14-}), but because the more ionic hydrogen is higher, the area

of strong potential shown in Figure 8a is less localized even than that of the CF₃ group.

Although electrostatics plays the dominant role, electron transfer between tip and surface is also present. This can be estimated by comparing the total Mulliken charge in the tip and in the surface as a function of distance, using the values at large distance (with no tip–surface interaction) as a reference.^{42,43} It is most relevant to the case of formate, where the formation of covalent bonds with the surface is more probable due to increased space between molecules. The electron transfer to the surface over bridging oxygen atoms amounts to 0.4 e in the most proximate point (–0.01 nm height), which is in close agreement with the prediction made on the clean TiO₂(110) surface.¹⁹ Moreover, the tip–surface transfer remains significant (0.15 e) when the tip approaches sideways to CH, and the molecule is forced to tilt. The major donating atom in this case is Si, and the accepting center is the nearest carbon. Notably, the electronic density associated with the molecule plus Si tip is still decreased by 0.1 e. The amount of electronic density spread in the substrate indicates depletion of the electron density at the point of contact. For acetate and 3F-acetate the electron transfer never exceeds 0.2 e at any site but is generally much smaller.

V. Discussion

In summary, we have shown that, for a dangling bond silicon tip, the strongest interaction is seen with the oxide surface rather than the organic monolayer. The interaction with the inert H or CX₃ groups is dominated by repulsion due to electron–electron overlap. The differences in force between the tip and formate and acetate and 3F-acetate can be explained by considering the effective coverage of the surface provided by the molecular groups. The H atom of formate is smaller and closer to the oxide surface than the other species, allowing increased access to the surface and, hence, increased attractive forces. Although the CH₃ group of acetate and the CF₃ group of 3F-acetate are structurally similar, the difference in bonding means that the electrostatic potential over CH₃ is much more delocalized, increasing effective coverage and reducing the interaction.

Before considering the general consequences of these results, it is interesting to apply them to the specific D-SFM experiments on similar systems discussed in the introduction.^{9–15} Experimental interpretation of images of formate, acetate, and 3F-acetate is based on the initial assumption that the molecules (either individual or as part of a monolayer) are imaged as bright. This then makes the interpretation of the individual formate molecules⁹ and ordered acetate layers¹⁰ straightforward. However, mixed layers of acetate and 3F-acetate showed two levels of bright contrast in images, with density matching the concentration of the two acids. The experimentalists suggested that this can be explained by the difference in dipole moments of the different molecules adsorbed on the surface, and our previous calculations³³ show that this could be true. Unfortunately, this interpretation of the experiments becomes much less clear when we introduce the tip into the system.

The experiments assume that the tip is silicon due to sputtering, but in that case, the results presented here remove the fundamental assumption behind all the interpretation: that the molecules are imaged as bright. If we assume a clean silicon tip and apply the interactions of Figures 3 and 6 we can get an entirely different analysis; bright spots in images of formate and acetate are now actually points of attraction between the molecular rows.

Another scenario to explain the results is that the tip is not clean silicon. One possibility is that the oxide layer was not

fully removed by sputtering. We modeled an oxidized tip by adding an oxygen atom to the apex of the silicon tip, in the process increasing the z dipole of the tip by a factor of 22. However, the interaction with the mixed layer remains generally weak, with an overall maximum over the bridging oxygen row; at no tip–surface distance does the interaction with acetate dominate. Other possibilities exist, such as strong localized charge at the apex or an adsorbed molecule on the tip; but without another source of information on the tip it is very difficult to find a good candidate. Beyond those specific experiments, our results indicate that a tip with a strongly localized positive charge at the apex is the best tip for imaging the molecules directly.

More generally, we have shown that imaging of organic layers with a dangling bond silicon tip may be significantly complicated by their inertness. Despite their projection of about 0.3 nm or more from the surface, there is no guarantee that they are imaged as bright. Really imaging the molecules requires special attention to preparation and control of tip properties. Preparation of functionalized tips could, for example, probe the surface hydrophobicity with high resolution.

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