Origin of the Contrast Interpreted as Intermolecular and Intramolecular Bonds in Atomic Force Microscopy Images

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ABSTRACT: The origin of the contrast in noncontact atomic force microscopy (NC-AFM) images, which is interpreted as intramolecular and intermolecular bonds, is still under debate. On the basis of the ab initio approach and explicitly including the tilt effect of the flexible CO tip, we reveal that the outermost electron density of the sample dominates the AFM contrast by corrugating the repulsive force that determines the frequency shift and the lateral behavior of the flexible tip. Consequently, we find that various aspects of bond images in AFM are governed by features of the electron density residing between nuclei; for example, in a π-conjugated system, the brightness of bonds is similar to that of atoms in AFM images due to the gently undulating π electron density; bright lines can arise between two bonded atoms (e.g., in a hydrogen bond) and also between "nonbonded" atoms (e.g., between two Xe atoms) due to the spatial overlapping of the outermost electrons.

1. INTRODUCTION

The use of a CO functionalized tip in noncontact atomic force microscopy (NC-AFM) operated in the frequency modulation mode1 has allowed unprecedented atomic resolution for imaging molecules.2–12 Not only can intramolecular bonds be distinguished,2 but images of hydrogen bonds have also been reported.8,13 However, there are still controversies about the origin of the AFM contrast between nearby molecules and even within individual molecules, which is interpreted as bonds. It has been proposed that the AFM contrast mainly comes from the Pauli repulsion between the CO tip and sample; the repulsive force is related to the electron density of the sample where greater electron density leads to a stronger repulsive force.14,15 However, M. Schneiderbauer et al. suggested that it is the electrostatic forces that dominate the AFM contrast rather than the Pauli repulsion.16 Additionally, the flexible CO used for imaging is tilting during scanning, which can distort the resulting AFM image so as to cause sharper features that look like bonds and also results in shift of the atom and bond positions.17,18 In contrast, recent studies have suggested that the flexibility of the CO tip plays the dominant role in causing intermolecular and even intramolecular contrast interpreted as bonds, which implies that the AFM contrast is only sensitive to the potential energy landscape originating from spherical symmetric potentials of the atoms while CO tilting produces sharp lines from the potential saddles between adjacent atoms that are arbitrarily interpreted as bonds.19,20

In this article, we apply a model that we have developed for two-dimensional AFM images, which explicitly includes the effect of the flexible CO tip, to explore the origin of the intermolecular and intramolecular contrast. We generate frequency shift (Δf) line profiles and two-dimensional force patterns for covalent bonds, the absence of bonds, hydrogen bonds, and π bonds, and also for molecules imaged in recent AFM experiments. With this systematic exploration, various features of the interatomic contrast are demonstrated, and the origin of the contrast interpreted as intramolecular and intermolecular bonds can be discussed.

2. THEORETICAL DETAILS

Our first-principle simulations are performed with the Fritz Haber Institute ab initio molecular simulations (FHI-aims) code package22 with grid-based real-space integration at "tight" setting. The FHI-aims tier 2 basis set (4s3p2d1f1g for N, C, O and 4s2p1d for H) is used throughout this work. Such an integration grid and basis set ensure that the calculated interaction energies are accurate at the meV level. The generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE)22 is used for the exchange–correlation functional for the DFT calculations. The DFT+vdW method of Tkatchenko and Scheffler (TS)23 is applied to account for the van der Waals (vdW) intermolecular interactions. In this work the vdW–TS scheme is performed as a total-energy correction to our preceding DFT calculations. Past studies in
the literature showed that the self-consistency in the vdW treatment has little effect on the structure and interaction energy.24

In our model,18 we use $\vec{R}$ to simulate the experimental results, where the $\vec{R}$ is the position of the macroscopic tip, which is measured experimentally, while $F_{Z\text{tilt}}$ is the force experienced by the O atom at its tilt-corrected displaced position. The two-dimensional $F_{Z\text{tilt}}$ force maps are calculated on a lateral grid of x and y positions with intervals of 0.2 Å. The $F_{Z\text{tilt}}$ force maps are calculated instead of the frequency shift maps because it has been observed that the contrast of the vertical force is the same as the corresponding frequency shift with a shifted scanning height ($H_{\text{scan}}$, the distance between the sample plane and O atom in CO tip) while greatly reducing the computational cost.5,18 The lateral spring constant of the CO at the metallic tip apex is set to be 0.4 N/m, which is a little larger than the experimental value of 0.26 N/m obtained with metal−CO25 because we used a linear relationship between the lateral force and the lateral oxygen displacement that is correct only for small tilt angles. The frequency shift $\Delta f$ is always obtained through26

$$\Delta f = -\frac{f_0}{2k_0} \left. \frac{\partial F_{Z\text{tilt}}(x, y, z)}{\partial z'} \right|_{z' = z}$$

where the interaction force $F_{Z\text{tilt}}$ already includes the CO tilting effect while the constants are $f_0 = 23$ 000 Hz and $k_0 = 1800$ N/m.5 Our simulated images are less sharp than the experimental images, and the distortion could be slightly overestimated due to several assumptions used.17 Nevertheless, the main features of the AFM images are reproduced very well and allow discussion of the intramolecular and intermolecular contrast.

3. RESULTS AND DISCUSSION

Assuming a flexible tilting CO tip initially oriented “vertically” (i.e., perpendicularly to the sample surface),2,27 AFM images are simulated as force maps of the “vertical” force component $F_{Z\text{tilt}}$. We show such $F_{Z\text{tilt}}$ maps (the third row of panels in Figure 1) for (a) a planar ethylene molecule with a covalent bond between the two C atoms, (b) two Xe atoms without an atomic bond, (c) two hydrogen fluoride (HF) molecules with a hydrogen bond, and (d) the π-conjugated molecule dibenzo-(cd,de)naphtho(3,2,1,8-para)perylene (DBNP). The $F_{Z\text{tilt}}$ maps obtained with a rigid tip28 are also shown for comparison with the $F_{Z\text{tilt}}$ maps to demonstrate the tilt effect.

The planar ethylene molecule with a covalent bond (1.33 Å, relaxed) between the two C atoms is shown in Figure 1a. The corresponding $F_{Z\text{tilt}}$ map shows that the maximum repulsive force appears at the midpoint between the two C atoms. By introducing the lateral tilt effect of the flexible tip, the single-maximum pattern is sharpened, and a faint contrast of the C−H
bonds in the form of shallow force ridges emerges in the \( F_{z}^{\text{nil}} \) map. The \( \Delta f \) profile along the C–C bond shows a single peak at the midpoint. Artificially increasing the C–C distance between the two CH\(_{2} \) groups to 2.33 Å (relative positions within each CH\(_{2} \) are unchanged), the \( \Delta f \) maximum is still located at the midpoint between the two CH\(_{2} \) groups. The single peak splits to two peaks when the C–C distance is increased to 3.33 Å, while the maxima are still in between and far from the positions of the two C atoms (marked by short vertical lines).

Clearly, the appearance of the maximum \( \Delta f \) at the middle of the covalent bond in ethylene cannot be simply understood as due to maximum interaction potentials on top of the C atoms and a saddle surface of potential in between, as proposed by references\(^{19}\) and \(^{20}\). However, the \( \Delta f \) maximum does correlate with the presence of enhanced electron density in the covalent bond region, which suggests that the intrinsic outermost electron density of the samples could be used to understand the AFM images. It has been proposed that the electrostatic forces dominate the AFM contrast,\(^{16}\) and hence, we could use only the electron density distribution from the sample while ignoring the Pauli repulsion to analyze the AFM contrast. In this work, we define the integrated outermost electron density (IOED), which is the integrated electron density ranging up to \( H_{\text{scan}} \) from a given height (\( Z_{\text{op}} \) above the sample plane). The lateral positions of IOED maxima shift dependent on the height \( Z_{\text{op}} \) and we chose the \( Z_{0} \) so that the lateral position of the global IOED maximum matches that of the \( F_{z} \) maximum. As demonstrated in the following, the IOED within the overlapping region between the tip and sample, which has been used in our previous work\(^{17}\) to understand the distortion in the AFM images, can well explain the AFM contrast.

The contour in Figure 1a reveals that the IOED maximum occurs above the midpoint of the ethylene and that shallow ridges appear along the C–H bonds, exhibiting an apparent relation with \( F_{z} \). When the two CH\(_{2} \) groups are artificially moved apart, we find that the outermost electron density tends to accumulate in between due to the strong attraction from the two C nuclei. This explains the change of the \( \Delta f \) when the C–C distance of the two CH\(_{2} \) groups increases to 2.33 Å. When the C–C distance is increased to 3.33 Å, less IOED is found in between than that above the C positions. However, the unsaturated electrons between the two separated CH\(_{2} \) groups yield a strong repulsive force on the CO tip, and the \( \Delta f \) maxima are still found near the midpoint. This is also the case for two isolated C atoms with a C–C distance of 3.0 Å (not illustrated here); a maximum \( \Delta f \) (or repulsive force) is found between the two C atoms in our ab initio simulations, in contrast to the two nearly circularly symmetric maxima in calculations without considering electrons in ref \( ^{20} \).

When two Xe atoms are placed together, the \( F_{z} \) map shows two nearly circularly symmetric maxima centered on top of the two atoms and a saddle surface in between, as shown in Figure 1b. The lateral force causes the CO to tilt away from the line connecting the Xe atoms. Consequently, the \( F_{z}^{\text{nil}} \) map including the tilt effect of the flexible tip produces a bright band connecting the two Xe atoms, yielding a bond-like contrast. With Xe–Xe distances of 2.5, 3.5, and 5.0 Å, the peaks of the \( \Delta f \) (or repulsive force) are always located close to tops of the Xe atoms. In the region between the two Xe atoms, the \( \Delta f \) corresponding to the bond-like contrast decreases with increasing Xe–Xe distance. When this distance is larger than 5 Å, \( \Delta f \) at the middle point is negligible, indicating that two isolated Xe atoms are then imaged in AFM.

The noble gas Xe is highly unreactive due to its full outer shell of valence electrons. When two Xe atoms are put together (e.g., by a high pressure), the outermost electron density overlaps in between them, which results in repulsion between the two Xe atoms according to the Pauli exclusion principle. We calculate that the total energy increases by 0.2 eV when the distance decreases from 5.0 to 3.5 Å. Although no bond is formed, the spatially overlapping electron density yields an IOED saddle surface between the two atoms, as shown by the contour map in Figure 1b. The IOED in turn causes a saddle surface of \( \Delta f \), sharpened by the lateral flexibility of the tip, and consequently results in bond-like contrast in AFM images. The electron density is highly localized at the atoms, and subsequently, \( \Delta f \) peaks are always centered on top of the two nuclei. As the distance between the two Xe atoms increases, the overlapping electron density in between decreases and finally vanishes, well explaining the change of \( \Delta f \).

In a hydrogen bond, the outermost electron density accumulates.\(^{29}\) When the two HF molecules get closer, more and more of their outermost electron density over-laps in between. The accumulated electron density results in attraction between the two HF’s; the total energy decreases by 77 meV when the distance decreases from 2.92 to 1.92 Å. For the HF dimer with a hydrogen bond of 1.92 Å, the accumulated electron density also results in an asymmetric saddle surface of repulsive force, as shown in the \( F_{z} \) map in Figure 1c. Due to tilting of the flexible tip over the saddle force surface, a bright band appears between the two HF molecules in the \( F_{z}^{\text{nil}} \) map (very similar to the nonbonding case of Xe–Xe shown in Figure 1b), which could be interpreted as the hydrogen bond. The HF dimer contrast is surrounded by a halo marked by deep blue due to the vdW attractive force.\(^{3} \) The H atom in the H–bond is invisible in the \( F_{z} \) map because electrons transfer to the nearest fluorine atoms, which is confirmed\(^{3} \) by the invisibility of H atoms in experimental AFM images bonding to elements with large electronegativity (e.g., in hydroxyl). The two \( F_{z} \) maxima correspond to the two fluorine atoms. The left \( F_{z} \) maximum is more “intense”, and its \( \Delta f \) is larger in value than that for the right fluorine (as best shown by the black curve). This is because the left fluorine atom has greater electron density than the right one whose electrons transfer partially to the hydrogen bond. By artificially increasing the distance between the two HF molecules, \( \Delta f \) between the molecules decreases finally to values similar to the halo, and the two \( \Delta f \) peaks become equal in value when the distance is larger than 3.9 Å. This is explained by the facts that the overlap of electron density decreases between the fluorine atoms and the electron densities on both fluorine atoms finally become equal when the two HF are separated.

The \( F_{z}^{\text{nil}} \) map shown in Figure 1d of DBNP agrees well with the experimental image, even in terms of the differences between bond lengths used to distinguish bond order.\(^{5} \) The hexagonal rings are clearly imaged, even though distorted, and maxima of the repulsive force are found along the periphery, all of which are seen in the experiment.\(^{5} \) In a \( \pi \)-conjugated system, the diffuse \( \pi \) electron density is spread out parallel to, and on either side of, the molecular plane of the nuclei, with a corrugation of maxima over the atomic positions and bonds, while minima occur over the hollow sites, just like the IOED contour shown in Figure 1d. The corrugation of the IOED matches the \( F_{z} \) map well, specifically as regards the distorted...
hexagonal rings and the periphery. This is further confirmed by the line profiles of IOED and $\Delta f$ along the red dashed line, which show essentially the same peak positions and relative peak heights.

The nonlinear relation between IOED and the tip–surface interaction force excluding the lateral tilt effect is complicated, as demonstrated in our earlier work.20 It depends on $H_{\text{scan}}$, the choice of the tip–sample overlap region for IOED, and the manner in which the vdW background is excluded. Nevertheless, direct comparison between IOED and $\Delta f$ without a lateral effect already uncover important information; the AFM contrast is apparently dominated by the outermost electron distribution of the sample. The AFM contrast indeed appears to originate in the outermost electron density of the sample, which yields the corrugation of the repulsive force, overlapped by the vdW attractive force and sharpened and distorted by the lateral tilt effect. The various AFM contrasts of the covalent bonds, or of the atomic bonds in the $\pi$-conjugated system, or between the atoms without or with an intermolecular bond are strongly correlated to the distribution of electron density accumulated between nuclei.

The results shown above can be used to understand recent experimental images.8 We show in Figure 2b the $F_{x}^{\text{dd}}$ pattern for two hydrogen-bonded 8-hydroxyquinoline (8-hq) molecules (with the structure shown in Figure 2a), which agrees very well with the experimental image, including for the two hydrogen bonds that can be identified as weak bands linking the molecules. The 8-hq molecules were computationally optimized on a Cu(111) surface until the forces were below 0.01 eV/Å, while the Cu(111) substrate was removed in the subsequent AFM simulations. The removal of the Cu(111) substrate excludes the effect from the substrate, so that the weak bond image can be fully attributed to the interaction between the two 8-hq molecules. In Figure 2c, we show that the electron density contour within an $x$–$z$ plane that cuts through the hydrogen bonds, as marked by the red dashed line in the $x$–$y$ plane shown in Figure 2a. Apparently, electron density accumulates within the hydrogen bonds between N and H (the two weaker outer local maxima are due to the nearby H within the OH groups). The electron density within a hydrogen bond is much smaller than that within covalent bonds or in $\pi$ bonds and therefore invisible in the total electron density maps, but they can be distinguished in electron density difference maps.13

The IOED shown in Figure 2d is integrated from 1.0 Å above the sample plane to $H_{\text{scan}}$. Peaks in the IOED corresponding to the hydrogen bonds yield ridges of repulsive force and result in brightness in AFM images that contrasts with the halo or vacuum away from the molecules. The $\Delta f$ across the hydrogen bonds obtained with a rigid tip exhibits a close relation to the IOED, while the two ends are markedly affected by vdW attraction. It is important to notice that the contrast of the hydrogen bonds of the 8-hq dimer is affected very little by the lateral effect of the flexible tip; the lateral force is very small across the hydrogen bonds due to the combined effect from lateral repulsion and vdW, and consequently, the $\Delta f$ line profiles obtained with a rigid and flexible tip are almost identical, as shown in Figure 2e.

Finally, we investigate a group of four bis(phenylpyridyl)-acetylene (BPPA) molecules that form a tetramer stabilized by hydrogen bonds while two N atoms are so close that bond-like contrast is observed in recent experimental AFM images.20 We computationally optimize the BPPA molecules on a Au(111) surface while the Au(111) substrate is removed in the subsequent AFM simulations. The optimized distance between the two closest N atoms is 3.25 Å (in the y-direction), which agrees well with the previous report,20 and the optimized distance between hydrogen-bonded N and H is 2.96 Å. The simulated $F_{x}^{\text{dd}}$ map in Figure 3a agrees well with the experimental image obtained with $z = 2.9$ Å, characterized by the bond-like contrast between the two closest N atoms, which is even brighter than the hydrogen bonds between N and H. An isosurface contour of the electron density shown in Figure 3b provides a visual impression that the outermost electron density in the region between the two N atoms is greater than that within hydrogen bonds; the 0.03 e/Å$^3$ isosurface between the two N atoms already overlaps while it is still much smaller at the midpoints of the hydrogen bonds. The electron density contours within the central $x$–$z$ plane shown in Figure 3d correspond to the cross section through the midpoint between the two closest N atoms, marked by the red dashed line in the $x$–$y$ plane shown in Figure 3c. Although it causes repulsion according to the interaction energy,20 the spatial overlap of the electrons between the two N atoms yields an electron density maximum and also an IOED ridge. As shown in Figure 3e, the corrugation of the $\Delta f$ obtained with a rigid tip exhibits a strong correlation with the IOED except that the two ends are affected by vdW interactions. Here, the ridge of $\Delta f$ is sharpened substantially by the flexible tip, and therefore, a bright contrast band arises between the two N atoms. Similarly, ridges of IOED and a repulsive force are found corresponding to the hydrogen bonds between N and H in the BPPA tetramer (not shown), yielding $\Delta f$ ridges that are sharpened by the tilt effect of the flexible tip.

![Figure 2](image-url)
Figure 3. (a) Simulated $F_z^\text{th}$ map at $H_{\text{scan}} = 3.1$ Å and (b) electron density isosurface for $0.03 \text{ e/Å}^3$ for the central part of a BPPA tetramer in the $x$--$y$ plane. (c) Chemical structure of the BPPA tetramer and (d) electron density contour of the center plane between the two N atoms in $x$--$z$ plane marked with a red dash line in (c). Over the same $x$ range along the red dashed line, (e) IOED integrated from $1.0$ Å above the sample plane to $H_{\text{scan}}$ and (f) $\Delta f$ line profiles obtained at $H_{\text{scan}} = 3.3$ Å with a rigid and flexible CO tip, respectively.

4. CONCLUSION

We have systematically studied the contrast observed with NC-AFM using CO functionalized tips for the cases of covalent bonds, “no bonds”, hydrogen bonds, and $\pi$ bonds by simulation with an ab initio approach. Our results for $\pi$-conjugated systems strongly suggest that the contrast is dominated by the outermost electron distribution of the sample. This result, which does not account for the Pauli repulsion from electron density overlapping between the tip and sample, confirms that the atomic contrast in the NC-AFM images originates from the short-range electrostatic force.\textsuperscript{16} In this work, we used the IOED, which is the integral electron density ranging from a given height above the sample plane up to the scanning height $H_{\text{scan}}$ and observed its apparent correlation with the repulsive force, which determines the frequency shift $\Delta f$ and lateral behavior of the flexible tip. Therefore, the similar brightness of the bonds to the atoms in a $\pi$-conjugated system is understandable in the AFM images, although the total electron density on atoms is much higher. The spatial overlap of electrons within intermolecular hydrogen bonds and between nonbonded atoms yields $\Delta f$ ridges. The $\Delta f$ ridges are usually (but not necessarily) further sharpened by the tilt effect of the flexible tip, which consequently yields more contrast in the form of bright bands between atoms that look very much like bonds. Therefore, it is challenging to distinguish between hydrogen bonds and no bonds in AFM images. Nevertheless, the direct identification of intramolecular electron redistribution by AFM would facilitate detailed investigations of intermolecular interactions in complex molecules with multiple active sites.

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Notes

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