Can STM be used to image molecules on surfaces?

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Abstract. The STM's ability to image adsorbates depends on the probability that the electronic states localized on the adsorbed molecule contribute to the tunnelling current. When the STM images are dominated by the substrate, any interpretation in terms of the actual positions of the atoms within the molecule is controversial. A criterion is presented for deciding whether an STM observation is of the adsorbed molecule directly or of the indirect effect of the molecule on the current from the substrate. It is based on analysis of the wave function associated with the tunnel current obtained by a self-consistent molecular orbital calculation, within the LCAO and cluster framework at CNDO level. The results for a range of molecules and polymers are in this case fully consistent with the criterion. The data suggest that any credible high-resolution STM observation of adsorbed species requires a contribution to the wave function not less than 50%. The notorious observed differences in contrast of co-adsorbed species are mainly attributed to considerable differences among individual contributions to the tunnel current.

1. Introduction

Despite a growing number of STM images claimed to be of adsorbed molecules, there is still a controversy as to whether or not those images are due to the molecular adsorbate or simply due to its effect on the image of the substrate. When molecules are adsorbed on a conducting substrate, the STM image of adsorbate–substrate system is usually different from that of the clean substrate. However, the interpretation of the new images in terms of the atomic structure of the adsorbed molecule can only be done with a high degree of confidence if the STM image is dominated by the adsorbate, otherwise interpretation is not straightforward. If the image is dominated by the substrate any change observed reflects the modification of the electronic structure of the substrate induced by the adsorbed species. In this case, there is no direct relationship between the changes in the STM image and the actual position of the adsorbed molecules, and a change in contrast can be wrongly attributed to the presence of the molecule. For example, previous calculations for CO adsorbed on Cu(100) surface [1] suggest an increase in the tunnelling current due to the substrate when the CO molecules move away from the tip under the action of the electric field of the tip. Despite considerable interest, the contrast mechanism in STM imaging of adsorbed molecules is not well understood.

Most STM images of adsorbed molecules are obtained in *constant current* mode, with the tip following a constant current contour. Because the wave functions of both electrodes fall off as $\exp(-r\sqrt{2m_e E_i/\hbar^2})$ (E_i is the binding energy of state φ_i and r is the distance from the electrode) at large distances, the tunnelling current is exponentially dependent on tip–sample separation. If the states localized on the adsorbed molecules do not contribute

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significantly to the tunnelling current the tip will approach the molecules in order to keep the current constant. Since the inter-electrode force is also exponentially dependent [2], the tip may then push the molecules along the substrate or plough through the molecules rather than image them.

The aim of this work is to propose a simple method based on the analysis of the wave function to predict the ability of STM to image adsorbed species. The results for a range of adsorbates successfully imaged by STM will provide a criterion for assessing the credibility of other STM images of adsorbed molecules.

2. Method of calculation

The LCAO representation of the tip–sample wave functions permits one to analyse the relative contribution of the adstates to the tunnelling current and thus to predict when the adsorbate observation by STM is probable. The only values possible for the tunnelling current of a tip–adsorbate–substrate system are the eigenvalues of the current operator I. In any measurement of the tunnelling current, the current operator I has the expectation value

$$I = \sum_i \langle \varphi_i | I | \varphi_i \rangle = \sum_i \sum_{\mu\nu} c_{i\mu}^* c_{i\nu} \langle \phi_\mu | I | \phi_\nu \rangle \tag{1}$$

where φ_i are the eigenstates of the tip–adsorbate–substrate system and ϕ_μ represent the atomic orbitals used in the expansion of the molecular orbitals. Assuming the zero-differential overlap approximation, we have

$$I = \sum_i \sum_\mu |c_{i\mu}|^2 I_{i\mu}. \tag{2}$$

The degree to which any atomic orbital ϕ_μ occurs in the expansion of the molecular orbital φ_i, measured by $|c_{i\mu}|^2$, determines the probability of obtaining the value $I_{i\mu}$ in a measurement of the tunnelling current. The measured current is then the sum of all atomic contributions. Since the aim is to obtain a simple and general criterion, the following approximations are introduced: (i) we assume a blunt tip so that it can be considered nearly planar over a small cluster of sample atoms; (ii) all the substrate atoms in that cluster are assumed to contribute equally to the tunnelling current; (iii) we assume that the molecular orbital localized on the adsorbate is collapsed into its centre of mass (for thick molecules or multilayers it is possible to relax this approximation in order to include spatial distribution of the atomic orbitals within the adsorbate); (iv) since under typical STM conditions the tip–sample interaction is weak, the expression for the tunnelling current based on Bardeen's transfer Hamiltonian formalism [3, 4]

$$I = \frac{2\pi e}{\hbar} \sum_{m,n} \left(-\frac{\hbar^2}{2m_e} \int (\varphi_n^{s*} \nabla^2 \varphi_m^t - \varphi_m^t \nabla^2 \varphi_n^{s*}) d\tau \right)^2 \{[1 - f(E_m)]f(E_n)$$

$$- [1 - f(E_n)]f(E_m)\} \delta(E_m - E_n + eV) = \sum_{m,n} \sum_{\mu,\nu} |c_{m\mu}|^2 |c_{n\nu}|^2 I_{\mu\nu}^{mn} \tag{3}$$

can be safely applied to the STM problem. Here φ_m^t and φ_n^s are eigenstates of the tip and sample Hamiltonians in absence of the other electrode, $f(E)$ are the Fermi functions ensuring transitions only from full to empty states and $\delta(E_m - E_n + eV)$ is an energy conservation factor which includes the tip voltage V as well as the individual state energies. Equation (3) shows that the current depends on the tip and sample atomic orbital amplitudes as well as their spatial distribution.

In the STM *constant current* operation mode the tip is scanned across the sample hovering at an approximately constant distance over the outermost atoms of the sample,

which contribute significantly to the tunnelling current. Therefore, when the tip is moving above a flat substrate where some molecules are adsorbed, the tip–substrate distance only increases at a molecule site, in order to keep the current constant, if the adstates close to the Fermi level dominate the tunnelling current (figure 1). Otherwise, the tip follows the substrate topography. Thus, the atomic orbital amplitudes will govern the contribution to the tunnelling current. Neglecting any spatial dependence within the adsorbate, we can predict the probability for imaging adsorbed molecules as

$$P_{\text{mol}} = \frac{1}{N} \sum_{i}^{N} \sum_{\nu}^{k} |c_{i\nu}|^2 \tag{4}$$

where k is the total number of atomic orbitals localized on the adsorbate and N is the number of molecular orbitals occupied (or unoccupied) which can be accessed by STM at a chosen voltage bias.
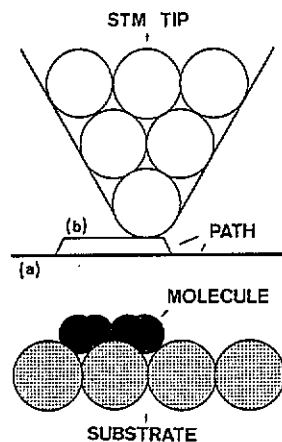

Figure 1. Schematic diagram of the STM tip path when the constant current image of the substrate–molecule system is dominated by: (*a*) the substrate and (*b*) the adsorbed species.
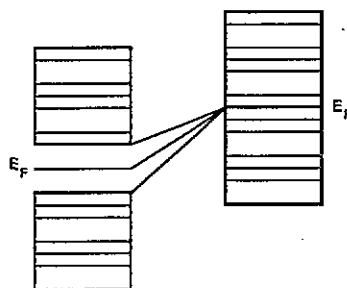
Figure 2. Schematic diagram of the procedure of correcting the gap and position of the Fermi level for the adsorbate–substrate cluster in order to match those of the macroscopic system.

The calculations reported here therefore comprise three main steps. The first concerns the calculation of an inhomogeneous electric field between the tip (modelled as a conducting sphere) and the substrate using the method described elsewhere [5]. The second includes this field in the self-consistent calculation of both electronic structure and molecular geometry of adsorbate–substrate system using the CHEMOS code [6], which combines molecular dynamics with the widely used CNDO molecular orbital method. These calculations were performed within LCAO and a cluster framework. The substrate is modelled as a layer of 16 metal atoms where a monolayer of molecules is adsorbed. The final step uses the self-consistent wave functions to estimate the probability for imaging adsorbed molecules by STM.

The metal substrate is supposed to screen the molecular adsorbates perfectly, therefore the Fermi level of the clean substrate should not change when the molecules are adsorbed. The bulk metal fixes the Fermi level of the entire system. Since the cluster calculation overestimates the gap between HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) and since the cluster Fermi level (defined as the mean of the HOMO and the LUMO) does not match the Fermi level of the macroscopic system, we have to change all one-electron orbital energies relative to the vacuum level in order to match

Table 1. Probability of adsorbate contribution to the STM current. Filled state and empty state images are obtained for positively and negatively biased tip, respectively.

System	Adsorbate contribution to STM image (%)	
	Filled state image	Empty state image
Polyimide/Ni(100)	58.3	84.4
Naphthalene/Ni(100)	50.8	33.9
Benzene/Ni(100)	34.4	52.3
CO/Ni(100)	14.3	33.3
Polythiophene/Ag(100)	12.8	47.7
t-polyacetylene/Ag(100)	0.8	3.0
Polypyrrole/Ag(100)	1.9	10.4
TTF/Ag(100)	3.2	14.1
TCNQ/Ag(100)	2.0	3.6
Pyridylsulphide/Cu(111)	1.6	1.3
Acrylonitrile/Al(111)	0.6	0.7

the experimental value for the Fermi level of the clean metal substrate and to eliminate the artificial gap arising between the HOMO and the LUMO (figure 2). However, no attempt has been made to correct the relative position of the states within the valence and the conduction band.

3. Results and discussion

Supposing that the tunnelling current can be kept constant to within 2%, we expect that the STM will be able to reveal only those adsorbates whose contribution to the tunnelling current is much greater than experimental error. Using equation (4) we have calculated the contribution to the tunnelling current for a range of adsorbed molecules and polymers successfully imaged by STM. The maximum adsorbate contributions to empty and filled state images were calculated, considering only states whose energy differ from the Fermi energy not more than 2 eV. The results are given in table 1. The contribution of the states localized on polyimide are illustrated in figure 3.

Some of the first high-resolution images of molecular adsorbates were those of (3×3) [7] and $c(2\sqrt{3} \times 4)$ [8] arrays of benzene molecules co-adsorbed with carbon monoxide. The only features clearly visible in both images resemble the form of benzene molecules. The CO molecules were invisible in the (3×3) structure but it was claimed they were seen in the $c(2\sqrt{3} \times 4)$ structure, though with low contrast. The non-observation of CO molecules in the first case was associated with molecular motion observed during the experiments. This suggestion is supported by the calculations of Ramos *et al* [1] which suggest the reorientation of CO molecules at low coverage induced by the STM tip. Our results for isolated molecules of benzene and carbon monoxide adsorbed on Ni(100) suggest that, in the case of co-adsorption, the STM image would be dominated by the adsorbate, and the benzene molecules would contribute 20% more than CO molecules. As a result CO would give less contrast then benzene. These suggestions are in agreement with the experimental data. More recently high-resolution images of naphthalene ($C_{10}H_8$) adsorbed on Pt(111) were reported [9]. The presence of an array of two-ball-like features in the STM images suggests the possibility that STM may be imaging individual naphthalene molecules. Our results for an isolated molecule of naphthalene adsorbed on Ni(100) surface show a molecular contribution of the order of 51% which supports the experimental findings.

All polymers considered in these calculations were imaged by STM [10–12], but high-resolution images were only obtained for polyimide. The lack of resolution was attributed
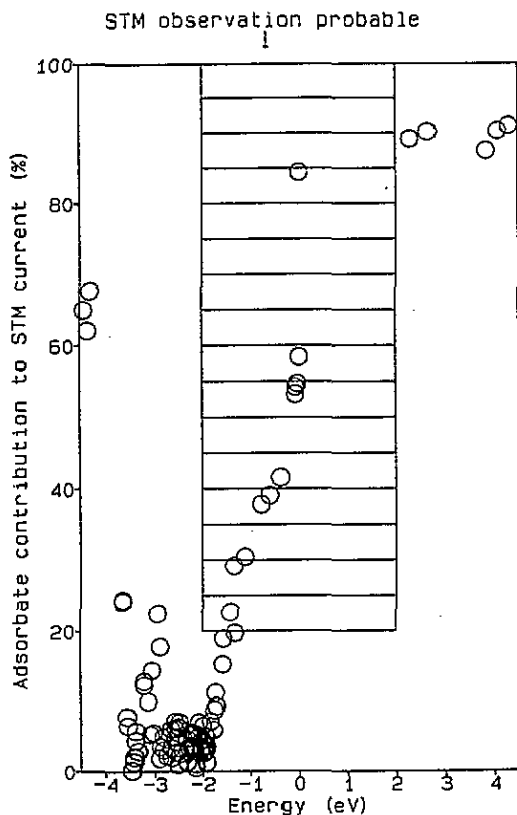
STM observation probable

Figure 3. Contribution of the electronic states localized on polyimide to the STM image of polyimide adsorbed on the Ni(100) surface. All energies are calculated relative to the Fermi level energy.

to high mobility of polymeric chains. Our calculations predict molecular contributions to STM current greater than 10% for all polymers. They also suggest that polyimide has the highest probability of being imaged by STM and polypyrrole the lowest. For polyimide, the results suggest an STM image clearly dominated by the polymer. The same is not so clear for the other polymers.

Another class of molecular materials that have been successfully imaged by STM includes the charge transfer complexes such as TTF–TCNQ [11, 13]. In the first images [13] only one type of feature could be identified. This feature was associated with the TCNQ molecules based on electronic charge distribution. Recent STM images were able to reveal two types of feature which were associated with both TTF and TCNQ molecules. As in the previous co-adsorption case, we have estimated the ability of the STM to reveal isolated TTF and TCNQ molecules on the Ag(100) surface. We should note that in these calculations we have neglected the significant charge transfer that occurs in the TTF–TCNQ complex which will probably affect the predictions. Our results suggest that both molecules contribute less than 15% to the STM current and the contribution of the TTF molecule is much greater than that of the TCNQ molecule.

Although no STM image has ever been attributed to acrilonitrile and pyridylsulphide, several successful images were obtained for a 4, 4′-bipyridyl disulphide on the Au(111) surface. Based on SERS spectra, Taniguchi *et al* [14] suggested that, in the process of adsorption, the disulphide bond breaks leading to the adsorption of pyridylsulphide molecules on the metal surface. The periodic uni-directional array shown in STM images of 4, 4′-bipyridyl disulphide was first attributed to pyridylsulphide molecules and later proved

to be due to the substrate [15]. Our results for acrilonitrile and pyridylsulphide show a probability of imaging these molecules lower than 2% which suggests that their STM images are unlikely to be due to the direct contribution of the adsorbed molecules.

These results suggest that for any credible high-resolution STM observation of molecular adsorbates the states localized on the adsorbed species should contribute 50% or more to the wave function giving rise to the current. If molecular contributions are lower than 10%, the STM images are likely to be dominated by the substrate. Finally we note that the contrast is bias dependent.

4. Conclusion

The method described here seems to be a simple and effective method to predict the ability of STM to provide direct information about adsorbed species. Generalizations can be made and would probably improve its accuracy. However, we believe the qualitative results to be reliable and these provide an insight into the STM contrast mechanism of molecular adsorbates.

All adsorbed molecules successfully imaged by STM present a contribution to the wave function greater than 10%, while high-resolution images have only been obtained for molecules showing a contribution greater than 50%. A contrast mechanism based on the relative contribution of all species is likely to explain the STM images of co-adsorbed species. However, the effect of molecular distortion and reorientation induced by the STM tip on contrast cannot be ruled out. The simplicity of this present criterion makes it ideally suited to be used by experimentalists. It provides a quick interpretation of STM images of adsorbed species based on physical principles rather than arguments based on considerations of the (unknown) symmetry of the adsorbed molecule.

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