J. Phys.: Condens. Matter 3 (1991) S127–S131. Printed in the UK

# Effects of the STM tip on adsorbate image

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Received 25 April 1991

**Abstract.** Scanning tunnelling microscopy provides atomic scale information about surface topography and electronic structure. However, the way the tip affects the STM image cannot always be neglected. We present a theoretical study of the effect of the non-uniform electric field of the tip on STM image of adsorbed molecules using Bardeen's approach. Self-consistent geometry optimization and wave-function calculations have been carried out within the CNDO approximation in a cluster model. Our results indicate significant effects. Thus for adsorbed CO on metal, the molecules reorient because of the tip, and the image is changed qualitatively as well as quantitatively. This may explain the lack of observation of CO at low coverage by STM. Our results also suggest the STM might be used for molecular modification.

## 1. Introduction

In spite of many attempts only a few STM images of adsorbates with atomic resolution have been reported [1, 2, 3]. This lack of sucess has been attributed to the poor conduction of the adsorbed molecules. However, this explanation cannot be used to interpret both the inability of STM to resolve individual CO molecules adsorbed on Pt(100) [4, 5] and its successful image of closepacked adlayers of CO on Pt(110) [6].

The aim of this work is to predict the effects of the STM probe on individual and assembled molecules adsorbed on metals, namely the electric field between tip and substrate, and assess the consequences for relating the tunnelling current to atomic positions. Our results show a considerable distortion and re-orientation of the adsorbed molecules the effects being stronger for highly polarizable molecules. In particular, the tip-induced re-orientation of CO at low-coverage causes a dramatic change in the tunnelling current which we believe to be a plausible explanation for its lack of observation by STM. We report here a self-consistent calculation of the adsorbate modification induced by the STM tip and a qualitative prediction of the STM ability to reveal those adsorbates.

## 2. Methodology

Since the basic theoretical approaches we follow have been already presented elsewhere [7], we note only the main steps of the calculation. It begins with the calculation of the inhomogeneous electric field between the tip and the substrate, and continues with the inclusion of this field in the self-consistent calculation of both electronic structure and

0953-8984/91/SAS127+05$03.50

molecular geometry of adsorbate/substrate system, using a semi-empirical molecular orbital method. The molecular orbital calculations were performed at CNDO level using a LCAO and a cluster model framework. The LCAO representation of the 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 final step is the estimation of the current by Bardeen's [8] tunnelling theory using the calculated wave functions and geometries.

We have extended our previous work by including the interations between adsorbed species and between those and the substrate, and also by considering other molecular species. In the calculation of the electric field a new term was added resulting from the interaction of the polarized molecules with each other and with both electrodes [9]. The chemical interaction of substrate atoms with adsorbates has also been included. The effect of the STM electric field on the adsorbed molecules will depend on the relative weighting of the simultaneous interactions between adsorbates (mainly dipole-dipole type) and their interaction with the substrate (mainly covalent type). The tunnelling matrix element involved in the expression of the tunnelling current is calculated over a planar surface. Since the LCAO construction of the sample wave-functions is inaccurate at large distances from the sample, a planar surface near the top of the adsorbed molecules was chosen.

## 3. Results and discussion

We have simulated the effects of a STM tip moving 6 Å above the top of isolated molecules of carbon monoxide (CO), acrylonitrile ($CH_2CHCN$), pyridylsulphide ($S{-}(C_5H_4N){\equiv}PyS$) vertically adsorbed at carbon, nitrogen and sulphur atom, respectively, on Cu(100), Al(111) and Cu(111) and also moving 6 Å above a submonolayer of CO on Cu(100). The applied bias voltage was 2 V (tip negative in the case of PyS and tip positive for the other molecules).

The effects predicted for acrylonitrile and pyridylsulphide were a rotation of these molecules by 15.3° and 3.5° respectively, and a distortion of the same molecules due to an increasing of C–C–C angle of acrylonitrile (figure 1) and a decreasing of the angle between the pyridyl ring and the sulphur atom 12° and 4° respectively. The acrylonitrile and the pyridylsulphide also showed a displacement of 0.6 Å and 0.1 Å towards the tip and the substrate, respectively. For the isolated CO molecule the effect predicted was a displacement of 0.2 Å towards the tip. The effects described above remain almost constant for the entire scan. The rotation, distortion and displacement of the molecules is mainly due to their interaction with the electric field. The distortion of large molecules can be explained in terms of the different atomic polarizabilities induced by the applied electric field, whereas in the case of small molecules like CO the effect predicted should be caused by the total molecular polarizability.

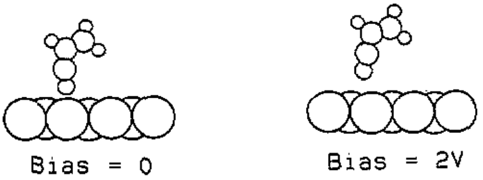

**Figure 1.** Effect of a STM tip of 9 Å radius at 9 Å above (i.e. centred 18 Å above) the Al(111) substrate on the geometry and orientation of an isolated adsorbed acrylonitrile molecule.

The polarizabilities predicted by CNDO are about 30% of the experimental ones and these do not always agree with charges transfer estimates based on electronegativity considerations. We expect greater distortion and re-orientation of polarizable molecules under STM measurements. Nevertheless, our results are a useful approximation of probable behaviour. We anticipate that there will be other organic molecules that may be modified by STM. Still greater effects like desorption and pinning molecules to the surface were observed for larger electric fields than those typical for STM imaging [10].

Our calculations showed that the contribution of CO to the tunnelling current is less than 20% while the contributions of acrylonitrile and pyridylsulphide are less than 3%. These results suggest that their STM images are unlikely to be due to the direct contribution of the adstates, with the probable exception of CO.

The predicted effects of a STM tip on a submonolayer of CO adsorbed on Cu(100) were the rotation and the molecular motion along the surface while the molecules remained bound to the substrate (figure 2(*a*)). The lateral displacement of the molecules can be understood by the following energetic considerations: Adsorption of an isolated molecule either onto the two-fold (initial) or four-fold (final) site gives a local energy minimum, both sites being stable in the absence of the tip. The electric field of the tip is sufficient to push the system from one type of site to the other, but only when the interactions between adsorbed molecules are included too. A combined electrical and force field has been used by Eigler and Schweizer [11] to move xenon atoms across the surface substrate. Zeppenfeld has used the same technique to move CO molecules around a platinum surface [12].

The change in atomic positions of CO cluster also causes a dramatic change in the tunnelling current (figure 2(*b*), (*c*)). The current was predicted for a bias voltage of 2 V as a tip of 9 Å radius scanned 9 Å above the substrate when molecular motion is either prevented or allowed. When the motion is prevented the total current shows one-bump structure centred at the CO site. The current due to the substrate also shows a one-bump structure slightly shifted relative to the adsorption site. When the molecular motion is allowed the bump associated with the central cluster molecule can no longer be distinguished. Moreover, the current shows some deep valleys probably due to interference effects resulting from changes in the electronic structure of the entire adsorption system.

We believe that the tip-induced distortion and molecular re-orientation is important in interpretation of the STM image of adsorbed species. We suggest that the induced molecular re-arrangement during STM measurements may explain the lack of observation of low-coverage adsorbed CO on metals by this technique. This suggestion is supported by the imaging sucess of high-coverage CO/Pt(110) [6], since in ordered layers the mobility of the adsorbates can easily be constrained by adsorbate–adsorbate interactions.

## 4. Conclusion

We conclude that any interpretation of STM measurements on adsorbed molecules should include the possibility of re-orientation and molecular distortion. Our results suggest that STM can be used as an important tool for surface modification on an atomic scale by manipulation of adsorbed atoms and molecules.

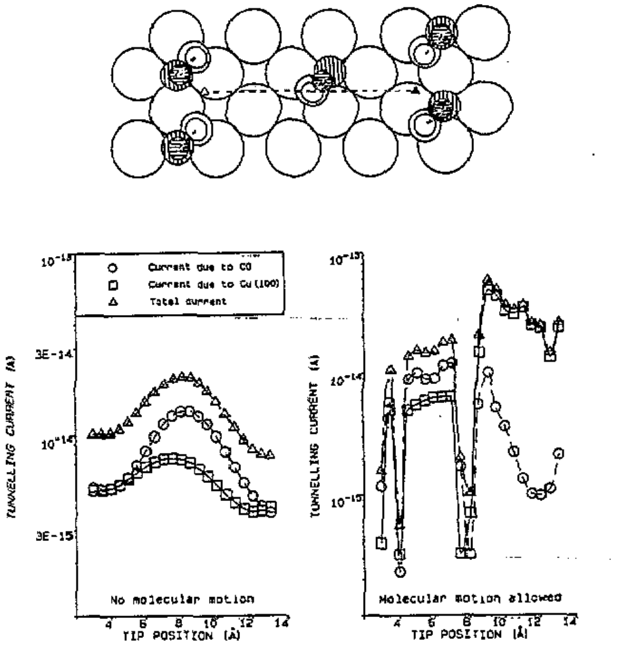

**Figure 2.** (*a*) Top view of the effect of the STM tip (radius = 9 Å, bias = 2 V) moving 9 Å above a Cu(100) surface where adsorbed a submonolayer of CO. The circles represent the atoms (large for copper, medium for carbon and small for oxygen), the marker represent the tip centre and the broken lines represent the path of both tip and individual atoms between the initial and the final (shaded circles) position. (*b*) Tunnelling current based on self-consistent wave-functions for optimized geometry with molecular motion forbidden. (*c*) Same as (*b*) with molecular motion allowed.

Whilst the methods of calculation used give approximate results, we believe that the qualitative results are reliable, and that the effects of the tip are important in relating STM images to atomic positions.

## Acknowledgments

One of us (MMDR) is indebted to the European Community for a Research Grant within the Stimulation Plan of the EEC.

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