



Trigonal images of transition metal atoms adsorbed on transition metal FCC (111) surfaces and their availability for scanning tunneling microscopy

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Abstract

We analyse the possibilities of using a scanning tunneling microscope (STM) as a complementary tool to a field ion microscope (FIM) for obtaining trigonal images of individual transition metal atoms adsorbed on atomically flat (111) surfaces of FCC transition metals. A calculation of STM images shows appreciable trigonal shapes. This should stimulate relevant experimental studies. Orientation of the images with respect to substrate atoms has been studied as a function of the character of adsorbed species and interpreted in terms of the calculated local density of states.

1. Introduction

In a series of papers [1–3], Wang and Ehrlich have reported trigonal shapes of the FIM spots produced by isolated transition metal atoms adsorbed on Ir(111) surfaces. The two possible orientations of trigonal spots with respect to the underlying lattice (Fig. 1) have been proven to depend on the species adsorbed. This behaviour has been explained [4] in terms of localised orbitals which are assumed to be directed towards the nearest missing neighbours in the corresponding adatom bulk structure, and act as trapping centres for the imaging gas. The phe-

nomenon of trigonal shapes is not the only one illustrating the concept of ‘localised orbitals as trapping centres’. Indeed, it has proved useful in explaining the regional brightness in FIM images around the (111) plane of an FCC structure and the alternating visibility and invisibility of ledges around the (0001) plane of an HCP structure [5]. At present, the most adequate tool for a local study of the electronic structure at the surface atoms is STM. Therefore, it is natural to ask about the feasibility of an STM study of the localized orbitals of these systems. Two questions arise, namely, if trigonal shapes can be obtained at all with STM, and if so, what would their orientation be, depending on the kind of adsorbed atom and on the type of adsorption site? In order to answer these questions we have carried out a quantum mechanical calculation of the electron structures and STM images of different atoms adsorbed on a Pt(111) plane.

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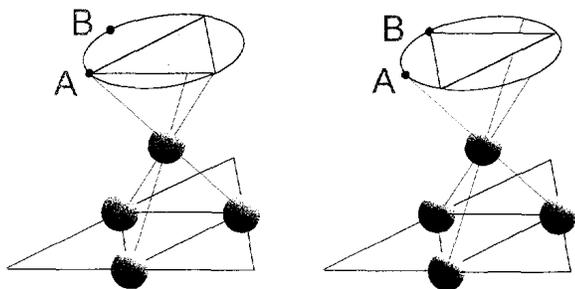


Fig. 1. Adatom and its three surface neighbours, with the two possible orientations of the trigonal image.

We have tried to include into our model all the relevant features which are necessary for obtaining a true description of the electron density distribution accounting at a qualitative level for the nature of the experimental results. The purpose of this calculation is to provide a qualitative picture of the obtainable images, and to account for their orientation along the row of the transition series. It is our intention to stimulate also the investigation in this direction, since there have been no systematic STM experimental studies until recently dealing with this topic. Moreover, even the FIM results do not cover systematically all the possible systems yet.

2. Computational procedure

The electronic structure has been obtained within a tight binding scheme. The local Green's function $G_i(w)$ is calculated in the usual way, by inverting the matrix $(wI - H - S(w))$, where H is the Hamiltonian matrix of the system formed by the adsorbed atom and its neighbours (Fig. 1), and w is the energy; the self-energy matrix $S(w)$ accounts for the effect of having a semi-infinite solid. It has been calculated by attaching Bethe lattices [6,7] to the atoms, forming the adsorption site, in the directions towards their nearest lattice neighbours. In order to take into account self-consistency we have applied a local charge neutrality condition [8]. This means that the energy levels of the adsorbed and surface atoms are shifted by a certain potential, such that the total charge at each atom is neutral (i.e. 10 valence electrons in a Pt atom, 9 in Ir, 6 in W and so on). The Hamiltonian elements have been taken from the values tabulated in Ref. [9] for the substrate atoms. The adsorption

position of the adatom is assumed to be unrelaxed, occupying the place that would be occupied by a lattice atom. We simulate the effect of different adsorbed species by imposing a different electronic occupation of the adsorbed atom. Then, within the charge neutrality assumption, we can characterize the behaviour of different adsorbates along a row of the transition metal (TM) series. This has been done for adsorbates with a number of valence electrons between 10 and 5, which corresponds to groups VIII B, VII B, VI B and V B.

The tunneling image was obtained using the Keldysh Green's functions formalism applied to LCAO Hamiltonians, in the way extensively described in Refs. [10,11]. This approach is well suited for tight binding calculations, and has the advantage that it is valid also for short distances, not involving any perturbative approximation. We have considered the low-voltage limit, in which the tunneling current is equal to the conductance times the applied voltage. In order to maintain the study at the most general level, the tip-apex atom has just one s orbital. The distance behaviour of the hoppings between the tip and the sample has been assumed to vary according to Harrison's formula [12]. This works optimally when the distance changes are not too large, which is actually the case (the distance between the tip and the adatom varies less than 25% for the range covered in the picture, which suffices for our qualitative characterization). The images obtained correspond to constant height scanings. The constant vertical component of the separation between the tip and the adatom is 0.67 nm, while the horizontal component reaches a maximum value of 0.56 nm at the edge of the picture.

3. Discussion of shapes and orientations

The obtained constant-height scanning images exhibit indeed an appreciable trigonal symmetry. Experimental confirmation of the observation of trigonal STM images of single Pt atoms adsorbed on a Pt (111) surface has been obtained recently [13]. The quoted study [13] concerned different topics and thus the orientation of 'triangular' images of the individual atoms, with respect to the underlying FCC lattice of the atomically flat (111) plane, has not been

estimated. However, the ‘triangular’ shape of the images of the deposited atoms on this plane has been clearly demonstrated in Ref. [13]. Calculation of the image for the two types of an adsorption site (bulk-like or surface-like, in the nomenclature of Ref. [1]) shows that the orientation is determined by the three adatom’s nearest neighbours. We can therefore avoid site specification when discussing the orientation of the spot relative to those three atoms (Fig. 1).

Results for different species are illustrated in Fig. 2. For adsorbed atoms with a high number of valence electrons (nine or ten), the orientation of the shapes coincides with that obtained by FIM, and also with the prediction in Ref. [4], provided that transition metals in the right-hand columns of the table form FCC lattices; the corners are located in the directions of a hypothetical FCC continuation of the lattice (points ‘A’ of Fig. 1). Similarly, the images of adatoms of groups VB through VIIB, having five to seven valence electrons, are oriented in opposite directions which again coincide with the FIM images and with the predictions suggested for FIM experiments in Ref. [4]; the corners are now pointing in the directions towards the three hypothetical BCC upper neighbours of the adatom (points ‘B’ of Fig. 1). The image corresponding to group VIIB is at the border

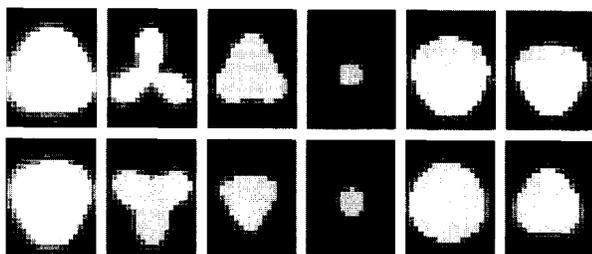


Fig. 2. Orientation of the calculated constant height STM images of isolated TM atoms, adsorbed on Pt (111). The upper row corresponds to ‘bulk’ (or FCC) sites, the triangle (being formed by the three adatom neighbours), points upwards. The lower row corresponds to ‘surface’ (or HCP) sites, with the substrate triangle pointing downwards. The number of valence electrons increases from five (left part of the figure) to ten (the right part of the figure), which corresponds to atoms of groups VB through VIIB (Ta, W, Re, Os, Ir, Pt). The brightest area corresponds to conductances higher than half the maximum, which for the scanning height considered attains nearly 0.05 au. When the tip is located just on top of the adatom their separation is 0.67 nm. The horizontal length of each image corresponds to 1.11 nm.

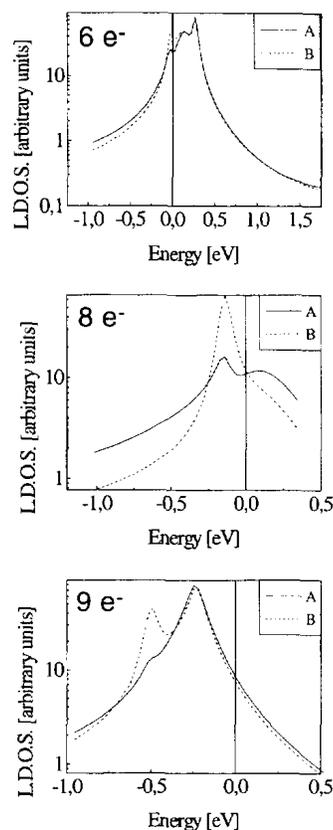


Fig. 3. Local density of states (LDOS) calculated at points A and B (Fig. 1), for three different adatom species containing six (on top), eight (middle) and nine valence electrons (below). Fermi level is always located at $E = 0$.

between both orientations, showing a round shape with no appreciable trigonality. This may or may not be the case for FIM too. Experiments, or a complete theoretical calculation of the field ionisation process (see below), would be able to elucidate this aspect. We can gain some insight into the qualitative comprehension of this phenomenon by looking at the local density of states at the two alternative positions A and B, as shown in Fig. 3. Despite the concrete details of individual curves, in all of them we can appreciate that to the right curve ‘A’ is higher than ‘B’, while there exists a region at the middle where curve ‘B’ is higher than ‘A’. A similar characterisation of the d density of states has been obtained in a different context by Van Santen [14,6], and used successfully to explain the adsorption site of CO and H on (111) TM surfaces. Therefore, in the case of

adatoms with a high number of valence electrons, the Fermi level is placed on the right-hand side of curves 'A' and 'B', where curve 'A' lies above 'B'. Consequently, higher current can be expected at points of 'A' type. For adatoms with a moderate number of valence electrons the Fermi level appears in the central region of curves 'A' and 'B'. The curve 'B' attains in this region higher values than the curve 'A' and thus a higher current at 'B' type points occurs.

FIM orientations, however, have the need for reactivity considerations, which involve the local density of states at all energies and not just at the Fermi level. The complexity is enhanced by the fact that the field ionization process takes place by tunneling of an electron from the probe atom (He) via field adsorbed atoms [4,15] (bound to the surface atoms by a 2p excited state [4,16]). Thus the reactivity would need a complete treatment involving non-trivial energy calculations, and taking into account explicitly the applied field and the quasi-chemical complex formed by the two He atoms involved in the field ionization (the field adsorbed one and the probe one). Nonetheless, the features of the LDOS depicted here remain at the basis of local reactivity considerations. Indeed, some theoretical studies have found a direct relationship (an approximate proportionality) between the LDOS at the Fermi level and local reactivity [6,14]. That is why a correlation between FIM and STM studies of these systems can be expected.

There is still a wide field to be explored in the characterization of localized orbitals as trapping centres. We have investigated the possibilities that STM has in this field. We have shown how it provides us with additional information, while imaging the system in the absence of a high electric field. The tip is believed not to modify chemically the surface, due to the larger tip-sample separation, though the tip itself can influence the image. On the other hand, FIM has just been for the investigation of reaction processes [17,18] and the directional orbitals played the role of trapping centers in these processes. It is then clear that an STM study of the directional orbitals of the system may help in understanding its subsequent behaviour under FIM conditions. On the experimental side, an STM study of a system treated here, or of the localized states mentioned in Ref. [5] (which are important in FIM for visualising how reactions pro-

ceed spatially [17]), would provide us with decisive information. Since STM results are complementary to FIM ones, any theory or model explaining the behaviour of such systems should be able to account for both kinds of results, at least qualitatively. With regard to FIM, the experimental results for a greater variety of transition metal adsorbates (and also substrates) would be desirable, in order to have a complete characterization of the trends in the image shape and orientation along the TM series. On the theoretical side, calculations treating explicitly the field ionization process would be useful for understanding the relative importance of the multiple effects involved in the FIM image in correlation with the chemical reactivity of the surface.

4. Summary

For a particular kind of adsorption system, we have analysed the directional properties of the local electronic density of states resulting from a tight binding calculation. Those directional properties determine the orientation of FIM as well as STM images. Our analysis relates that orientation to the number of valence electrons of the adsorbed species, and consequently to its group in the periodic system. In this way it is also related to the structure in which it crystallises. STM images of adsorbates (FCC metals) with 9–10 electrons would show a reversed orientation with respect to those with 5–7 electrons (BCC or HCP metals). These results coincide with the predictions based on experimental FIM images. The border between both orientations is obtained when the adsorbate has 8 valence electrons, showing a round shape with no appreciable trigonality. Calculations of FIM images, and systematic experiments covering a wide range of adsorbates, both by FIM and STM, would provide valuable information for understanding the nature of localized states at transition metal surfaces and their role as trapping centres for catalytic processes [18].

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