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Analytical Applications of Scanning Tunneling Microscopy

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Analytical Applications of Scanning Tunneling Microscopy

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Abstract

Recent progress and applications of scanning tunneling microscopy and scanning tunneling spectroscopy in molecular identification are presented. In particular, the difficulties in the direct interpretation of images are elaborated. The current limitations as well as the potential of this technique are discussed.

Introduction

Since its development in 1981 [1], the scanning tunneling microscope (STM) has proven useful in many fields including surface science [2], low temperature physics [3], and electrochemistry [4]. The STM is now one of several proximal probes which are based upon scanning a tip with extremely high resolution at atomic scale separations from surfaces. These techniques utilize a short range interaction between the probe and the surface for feedback control of the tip–sample separation. In scanning tunneling microscopy, the interaction is the tunneling current between the tip and sample when a voltage bias is applied between them. The tip–sample separation and the lateral tip position are controlled using piezoelectric translators. Related techniques which were developed subsequent to the STM include atomic force microscopy [5,6], near–field optical microscopy [7], and a plethora of others [8]. Analytical chemistry applications of all these techniques remain in their infancy. The STM has the capability to image individual atoms on many crystalline surfaces that are either clean or covered with an ordered overlayer of atoms. As discussed below, the STM has had more limited success

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with disordered overlayers and isolated adsorbates. Developing a means to distinguish between different molecules and molecular features remains the central issue inhibiting the use of the STM as a standard analytical tool. One method proposed for this purpose is scanning tunneling spectroscopy. I note that a nearly identical statement appeared in the last *Trends* article on STM [9], and progress in tunneling spectroscopy since then has been rather limited.

The focus of this article is to describe progress in the use of the STM in identifying single atoms and molecules. The great advantage of such an ability would be that the STM records data in real space, is non–destructive, and is relatively simple and inexpensive to operate. Additionally, the STM can be used in the limit of low surface coverage, *i.e.* with small total numbers of molecules. A number of excellent reviews are available on STM imaging [10–12] and instrumentation [11,13], scanning tunneling spectroscopy [10–12,14], and related techniques [6,10–12].

Contrast in STM Imaging

Contrast in imaging is the ability to distinguish between different objects. Here we consider obtaining contrast between different atomic or molecular adsorbates and the atoms of the substrate surface. The mechanism of imaging adsorbates is not entirely understood, so that optimizing, understanding, and even obtaining such contrast remains elusive.

An example of the difficulty in obtaining interpretable images with the STM can be found in the work of Wilson and coworkers on Cu–phthalocyanine on Cu{100} [15]. The images obtained were compared to theoretical calculations, and good agreement was obtained. However, images were also obtained on the same surface which appeared to agree with the calculations, but could not be reconciled with the known molecular orientation, and were attributed to tip artifacts.

Another example of the difficulty in understanding STM images comes from observations of benzene molecules adsorbed on various surfaces. In the work of Ohtani *et al.*, benzene and CO were coadsorbed on Rh{111} in order to hold the molecules rigidly in an ordered overlayer [16]. The observed features attributed to benzene consist of three lobe structures in the STM images. Weiss and Eigler have imaged isolated benzene molecules on Pt{111} at low temperature (4K), and have observed three different types of images depending upon the adsorption site of the benzene [17]. Examples are shown in Fig. 1 taken from ref. [17]. The images in the upper, middle, and lower frames of Fig. 1 were assigned to: a three–fold hollow site, an atop site at or near a defect, and a bridge site, respectively. The site assignments were made by: comparing these images to previous data, comparing the frequency with which the different sites were found under different absorption conditions, and comparison with the detailed calculations of chemisorption energies and STM images by Sautet and Bocquet [18]. Calculations of STM images of adsorbed benzene on metal surfaces have predicted a number of varying images depending upon the surface, the adsorption site, the metal Fermi level, and the tunneling conditions [18–20]. Some of these predictions have been borne out experimentally. The calculated images of benzene on Pt{111} by Sautet and Bocquet illustrate many of these features and also show the complexity of the situation in which different molecular electronic states interfere to produce the images found [18]. Only a very small number of STM images of molecular adsorbates are understood on a quantitative basis.

Wolkow and coworkers have imaged benzene on Si(111). In their data, the adsorbed benzene molecules appear only to enhance the tunneling to Si substrate atoms, and thus appear as three bright spots in topographic images [21]. The situation is generally complicated on semiconductor surfaces because the semiconductor surface electronic structure appears to dominate all other features. Adsorbates on semiconductor surfaces have often been observed only as spectroscopic changes in the semiconductor substrate images [22].

Recent progress on semiconductor surfaces has been made by Boland and by Hamers and coworkers who have used a combination of STM imaging, spectroscopy and adsorption site coordination in order to identify hydrogen at various sites and reacted disilane fragments on the Si(100) surface [38,39]. These reaction products include H, SiH_2 and SiH_3 [38,39]. For example bright spots in images at bridge–bonded positions are inferred to be SiH_2, whereas adsorbates appearing at dangling bond sites are attributed to SiH_3 [39]. These assignments are corroborated by observing the reaction of these species, such as metastable adsorbed SiH_3 apparently fragmenting into adsorbed SiH_2 and H. Nonetheless, there remain disagreements as to some of these assignments.

Hallmark and Chiang have imaged a series of aromatic molecules: naphthalene, azulene, and a number of substituted azulenes in order to compare images of closely related molecules to each other and to theoretical calculations [23]. One technique they have used to distinguish between coadsorbed molecules is thermally activated motion of some of these species as a means of differentiation. An example is shown in Fig. 2 from ref. [23] where naphthalene and azulene have been coadsorbed on Pt{111}. Two rings are apparent in the image for naphthalene molecules as when naphthalene monolayers are imaged without coadsorbates on the Pt{111} surface. An azulene molecule, highlighted with a circle, appears as a single ring in this image and also appears this way in monolayer coverages on the same surface. In this case, the difference between the shape of the azulene molecule in the images and the known molecular shape is attributed to rotation of the azulene molecules faster than the time scale during which they are imaged [23].

Some of the elements at the surface of a decagonal quasicrystalline Al–Co–Cu alloy could be identified by Becker and coworkers using arguments based upon stoichiometry and atomic spacings [24]. They were unable, however, to identify the surface atoms of a more complicated icosohedral quasicrystalline alloy structure [24]. More recently, other surface atoms, Pt and Ni have been differentiated in the surface layers of solid alloys with known surface compositions, but only under special STM tip conditions that could not be reproduced at will [25]. Besenbacher and coworkers have shown that by placing an O atom at the end of a W STM tip, they could image only the overlayer metal atoms in ordered overlayers of O on Cu{110} and Ni{110}, whereas with a nominally clean W STM tip, they imaged the overlayer O only [26]. This is shown in Fig. 3 taken from ref. [26] in which the left plate shows the surface imaged with a nominally clean W STM tip and the right plate shows the surface imaged with an STM tip with a terminal O atom. The grid marks correspond to the positions of the Ni atoms in the substrate 1x1 layer underneath the Ni–O adlayer.

Artifacts in images have been shown to be a particular problem when using graphite as a substrate [27]. Features apparently present in images of the bare graphite at steps and other defect sites have been attributed to or bear similarity to what was expected in the images of the molecules under study. The ease of use of graphite, due to the simplicity of cleaving it, and the ability of many instruments to obtain atomic resolution images of it in air made it seem to be a near ideal substrate. A very large number of STM studies of adsorbates to date have used graphite as a substrate despite the drawbacks noted above.

An alternative approach to the identification of part of a molecule was taken by Barton, Lieber, and coworkers using advances from the rapidly developing field of site–specific binding on DNA and other macromolecules [28]. In preliminary work, a metal–containing small molecule which binds site–specifically is attached to DNA in order to mark a spot along the DNA molecule [28]. Tunneling is enhanced at this attachment site and it appears as a protrusion in STM images. While such a technique is not expected to be competitive with sequencing methods such as fluorescence tagging

[29], there may be special applications where one can determine the site at which a molecule binds to a large molecule such as DNA without the need to obtain an X-ray crystal structure.

Spectroscopy of Single Molecules

Although scanning tunneling spectroscopy has been in use for more than five years [14,30], its use in distinguishing unambiguously between different adsorbates has not been demonstrated. Perhaps the result closest to this goal was the differentiation of Ga and As in the GaAs(110) surface by Feenstra and coworkers [31] (and subsequent work on other III–V semiconductors).

Theoretical work by Lang has shown that it is possible in principle to distinguish between adsorbates using imaging and spectroscopy for the case of atomic adsorbates on (model) metal surfaces [32]. This would be done by scanning the sample bias over several volts at positive and negative bias corresponding to resolving the electronic structure of the adatoms up to several eV above and below the Fermi level, respectively. While adatoms have not yet been distinguished experimentally using this technique, two recent measurements have demonstrated aspects of this method. First, images obtained of isolated Xe atoms on Ni{110} and Pt{111} have shown that the models used by Lang and others are quantitatively correct [33]. An example of the difference predicted for images recorded at low bias of Xe and He along with a measured line scan across a Xe atom on Ni{110} is shown in Fig. 4 adapted from ref. [33]. Second, Eigler and coworkers have recently demonstrated that the electronic structure of the STM tip (which also contributes to the tunneling spectrum recorded) can be removed so as to be able to measure the electronic spectrum of a single adsorbate. This was done for Fe adatoms on Pt{111} [34].

Hashizume *et al.* have shown that by changing the admixture of electronic states accessed by recording images as a function of bias voltage, the appearance of an adsorbate changes dramatically [35]. This type of bias dependence was predicted by Fisher and Blöchl [20] for STM images of benzene molecule. Sautet and Bocquet have shown that the direct comparison of STM images to calculated molecular orbitals can be dangerous because of complicated interferences between the contributions of these different orbitals [18]. This will certainly be the topic of many future studies involving the bias dependences of STM images of molecules, and may yet provide the link allowing identification of molecular adsorbates.

Various schemes have been proposed for using other than electronic structure to identify and study individual adsorbates. One example would be the use of inelastic tunneling for recording vibrational spectra of adsorbates [36] in analogy to inelastic tunneling in sandwich tunnel junctions [37]. The inherent problems with these measurements are the small signal levels expected which lead to extreme requirements for detection in order to observe the expected signals.

Conclusions

There currently exist no methods to identify molecules and to distinguish between molecular features with the STM. Several methods using scanning tunneling spectroscopy may allow this in the future. A fuller understanding of molecular imaging with the STM also may allow its more fruitful use as an analytical tool. Experiments and theory have pointed out that the substrate, the adsorption site, the STM tip, the tunneling parameters, and the interferences of the electronic states which determine the tunneling current all play important and not entirely understood roles in determining the STM images and spectra of surface species. Through the close coupling of theory and controlled experiments we hope to develop a predictive understanding of STM images and spectra of adsorbates to allow analytical uses of the STM.

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Figure Captions

1. Images of three different benzene on Pt{111} recorded at low temperature (4K) in ultrahigh vacuum. All of the images were recorded at low, negative tip bias, and are 15Åx15Å. The molecule in the bottom image appears 1.0Å high and all the vertical scales are the same. The image is reproduced from ref. [17], courtesy of the AIP.

2. STM topograph from ref. [23] showing naphthalene (highlighted with ellipses) and azulene (highlighted with a circle) coadsorbed on the Pt{111} surface. The molecules are distinguished on the basis of their shapes. The azulene is believed to appear as a circle because of rotation that is fast compared to the time scale used for imaging. This image is reproduced from ref. [23], courtesy of V. Hallmark and S. Chiang.

3. The left plate shows a 37Åx47Å area of the O/Ni{110} surface imaged with a nominally clean W STM tip and the right plate shows the same surface imaged with an STM tip with a terminal O atom. The grid marks correspond to the positions of the Ni atoms in the substrate 1x1 layer underneath the Ni–O adlayer. These images are reproduced from ref. [26], courtesy of F. Besenbacher and coworkers and the AIP.

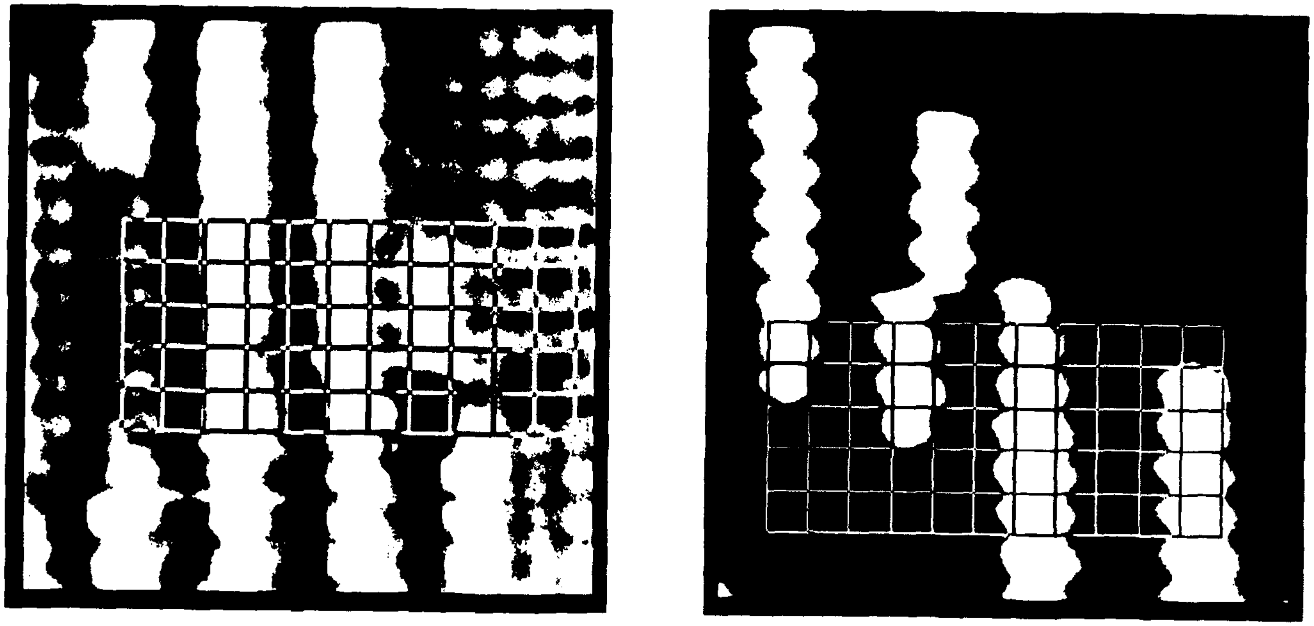
4. The solid lines show calculated line scans of tip height vs. lateral position for imaging Xe and He on a jellium surface with charge density comparable to Ni. Superimposed is a line scan recorded for a Xe atom on a Ni{110} surface. This figure is adapted from refs. [32,33].

5. STM images recorded of a 22Åx22Å area of a C_{60}–covered Cu{111} surface at sample bias voltages of: a) $^{-}$2.0V, b) $^{-}$0.10V, and c) 2.0V, respectively. These images are interpreted as being dominated by the molecular orbitals depicted in Fig. 6. These images are reproduced from ref. [35], courtesy of T. Hashizume, T. Sakurai and coworkers and the AIP.

6. Local density of states calculated to correspond the STM images shown in Fig. 5, and centered at energies of $E-E_f=$ a) $^{-}$2.0 eV, b) 0 eV, and c) 2.0 eV, respectively. This figure is reproduced from ref. [35], courtesy of T. Hashizume, T. Sakurai and coworkers and the AIP.

Weiss Fig. 1 UP^

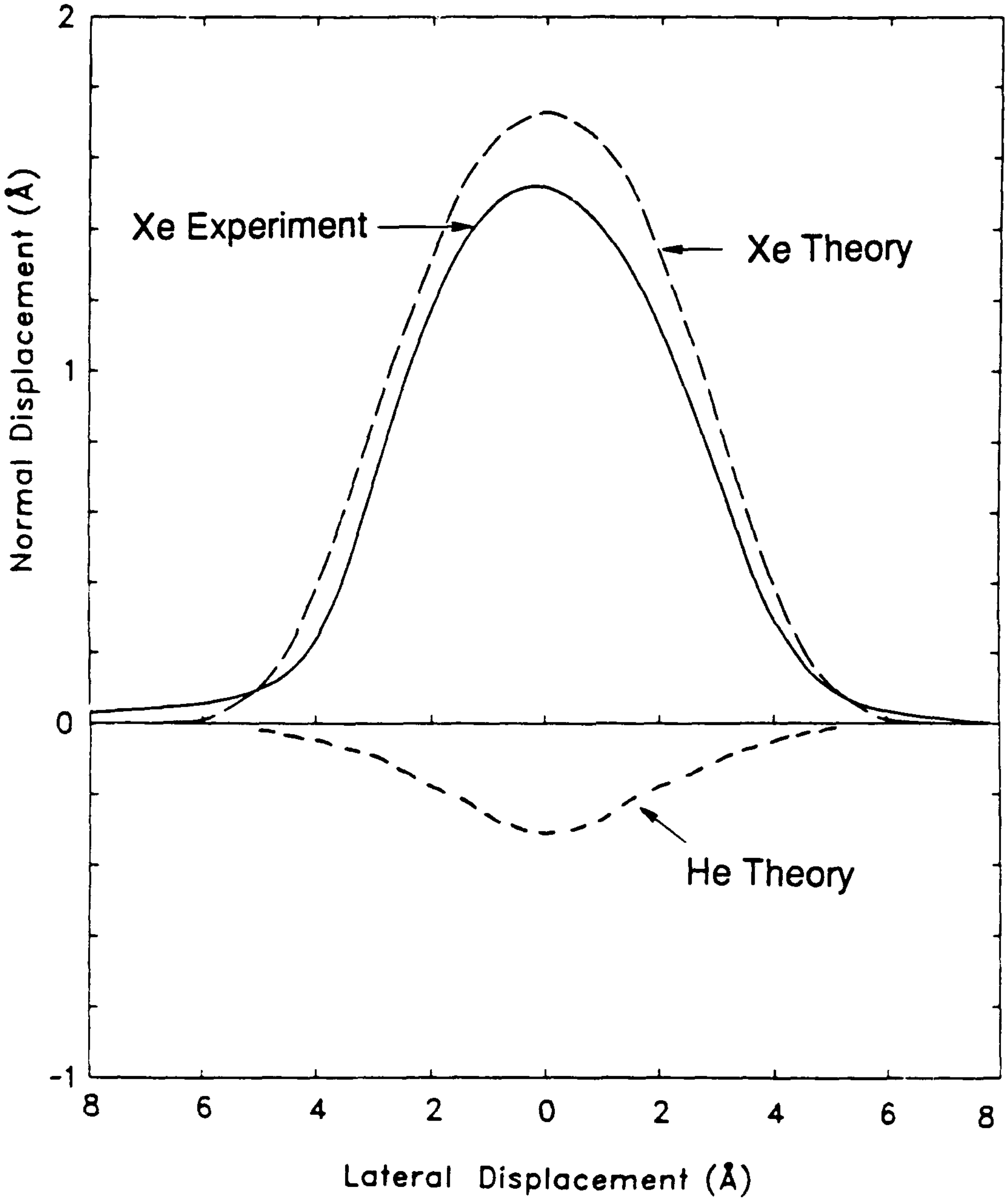
Weiss Fig. 2 UP^



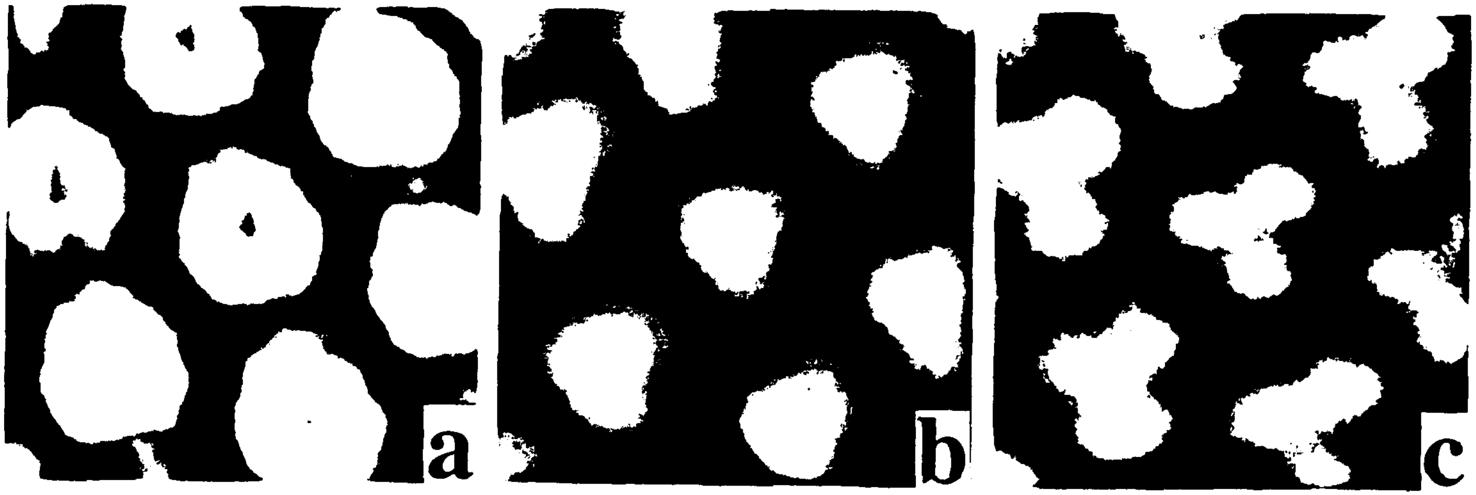
W tip

O tip

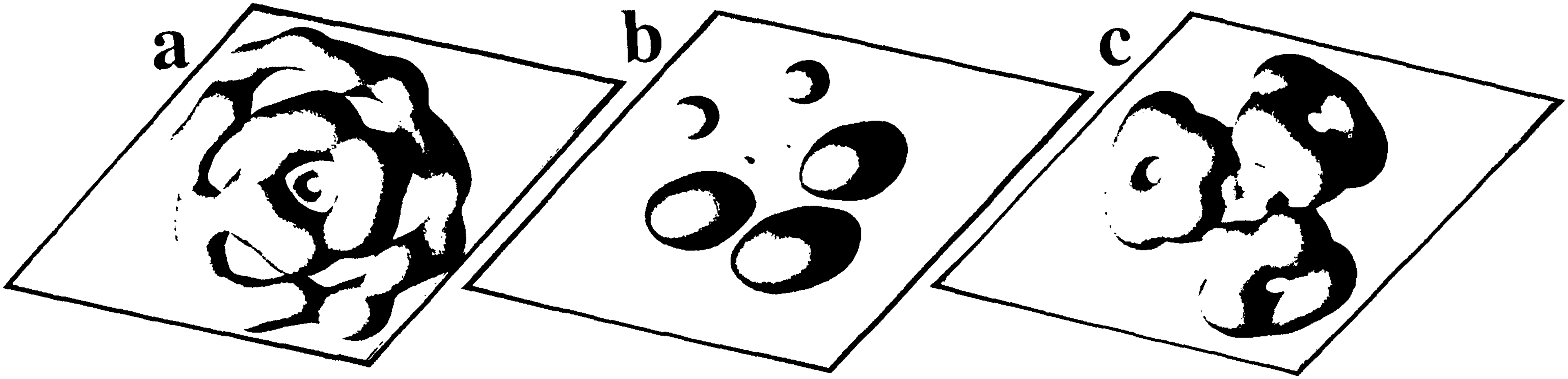
Weiss Fig. 3 UP^



Weiss Fig. 4 UP^



Weiss Fig. 5 UP^



Weiss Fig. 6 UP^