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Surface Science 454–456 (2000) 1079–1084
surface science
www.elsevier.nl/locate/susc

Controlled lateral manipulation of single diiodobenzene molecules on the Cu(111) surface with the tip of a scanning tunnelling microscope

S.W. Hla *, A. Kühnle, L. Bartels [1], G. Meyer, K.H. Rieder

Institut für Experimentalphysik, Freie Universität Berlin, Arminallee 14, D-14195 Berlin, Germany

Abstract

We report on the controlled lateral manipulations of adsorbed single diiodobenzene molecules on the Cu(111) surface with a scanning tunnelling microscope (STM) tip at 20 K. The molecular motions in this experiment are mainly induced by the attractive interaction between the tip and the molecule. Even though the leading manipulation mode is 'pulling', a continuous 'sliding' mode can also be induced if we use higher tip–molecule interaction forces. During the manipulation process, the molecules can follow the tip with hops of single or double copper-atomic-site distances and in some cases 'hop-scotch' type movements can also be observed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Aromatics; Chemisorption; Copper; Scanning tunneling microscopy

The recent advances in atomic and molecular manipulation on crystal surfaces have created a new exciting era in nanometre-scale science and technology [1]. By employing tunnelling electrons, the dissociation and rotation of single molecules can be performed [2,3]. By using vertical manipulation techniques, single atoms or molecules can be transferred between the tip of a scanning tunnelling microscope (STM) and the surface in a controlled manner [4,5]. With the STM tip, one can also write letters with atoms and molecules [6], move adsorbates to desired locations on the surface [7] or reconstruct the native surface on an atom-by-atom basis [8]. This kind of atomic or molecular motion is known as lateral or 'soft' manipulation, and utilises the forces acting between the STM tip and the adsorbate [5,9]. Three manipulation modes can be distinguished in this regime: in the 'pulling' mode the adsorbate follows the tip movement due to the attractive interaction between them; in the 'pushing' mode the adsorbate moves in front of the tip because of their repulsive interaction; and in the 'sliding' mode the adsorbate is trapped under the tip during the motion. Atomic-scale precision, extreme stability of the system and very fine control over the local tip–molecule–surface interactions are necessary ingredients for a successful lateral movement. While the lateral manipulation of large molecules can succeed at room temperature [1], the manipulation of smaller ones such as CO has to be performed at

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* Corresponding author.
E-mail address: hlas@physik.fu-berlin.de (S.W. Hla)

[1] Present address: Columbia University, CRL/MSL MC 8903, New York, NY 10027, USA.

PII: S0039-6028(00)00072-8

lower temperatures in order to minimise their thermal motion on the surface. The beauty of these lateral manipulation techniques is that not only can the molecular movements be controlled with atomic precision, but also information about local tip–molecule–surface interactions and molecular diffusion dynamics during the lateral manipulation on the surface can be extracted. The motivation for the current work was based on the artificial creation of a halobenzene diffusion process on copper surfaces, which is one of the elementary steps of the Ullmann catalytic reaction [10]. 1,4-Diiodobenzene has been chosen as the candidate for this particular experiment owing to its usefulness in chain formation under the Ullmann-type reaction, which may lead to the formation of future man-made molecular wires.

The experiment was conducted in a home-built liquid-helium-cooled ultrahigh vacuum (UHV) STM [11] at the base pressure of 4×10^{-11} Torr. The STM imaging was in constant-current mode and an electrochemically etched polycrystalline tungsten tip was used throughout the experiment. The tip was prepared in situ by gently touching the copper surface prior to each experiment. The Cu(111) sample was cleaned by repeated cycles of sputtering with neon ions followed by annealing up to 800 K. 1,4-Diiodobenzene ($C_6H_4I_2$) (Aldrich, 99%) was purified by several pumping cycles and dosed in small amounts through a tiny aperture in the radiation shield of the STM. This allows the controlled dosing of gas species down to very small (~0.001 ML, where ML = monolayer) coverages on the sample surface. The sample temperature during the entire experiment was fixed at 20 K.

A typical STM image of the Cu(111) surface after deposition of a small amount of diiodobenzene molecules at 20 K is shown in Fig. 1. A few molecules are randomly adsorbed on the plane terrace and some are anchored at the step edges.

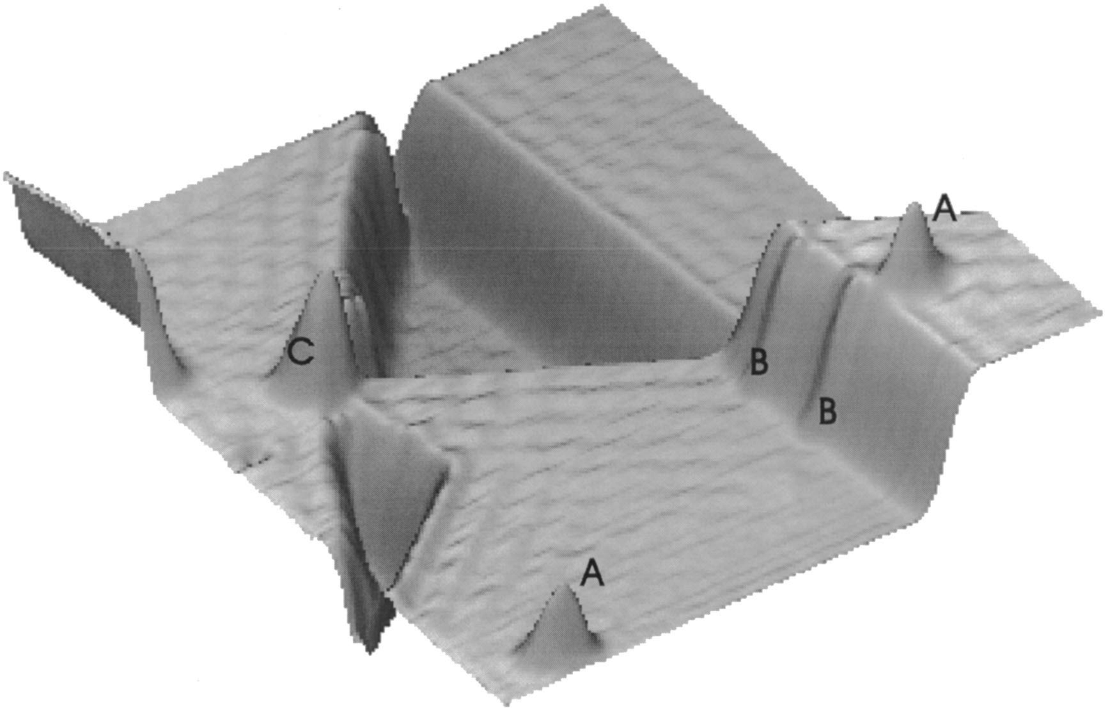

Fig. 1. 80 Å × 80 Å scan STM image of the Cu(111) surface showing adsorbed diiodobenzene molecules together with background standing-wave patterns caused by step edges and the adsorbed molecules. A, adsorbed molecules on the terrace planes; B, adsorbed molecules at the lower part of a monoatomic step edge; C, a molecule adsorbed at a defect site ($V_t = 200$ mV, $I_t = 1.3$ nA).

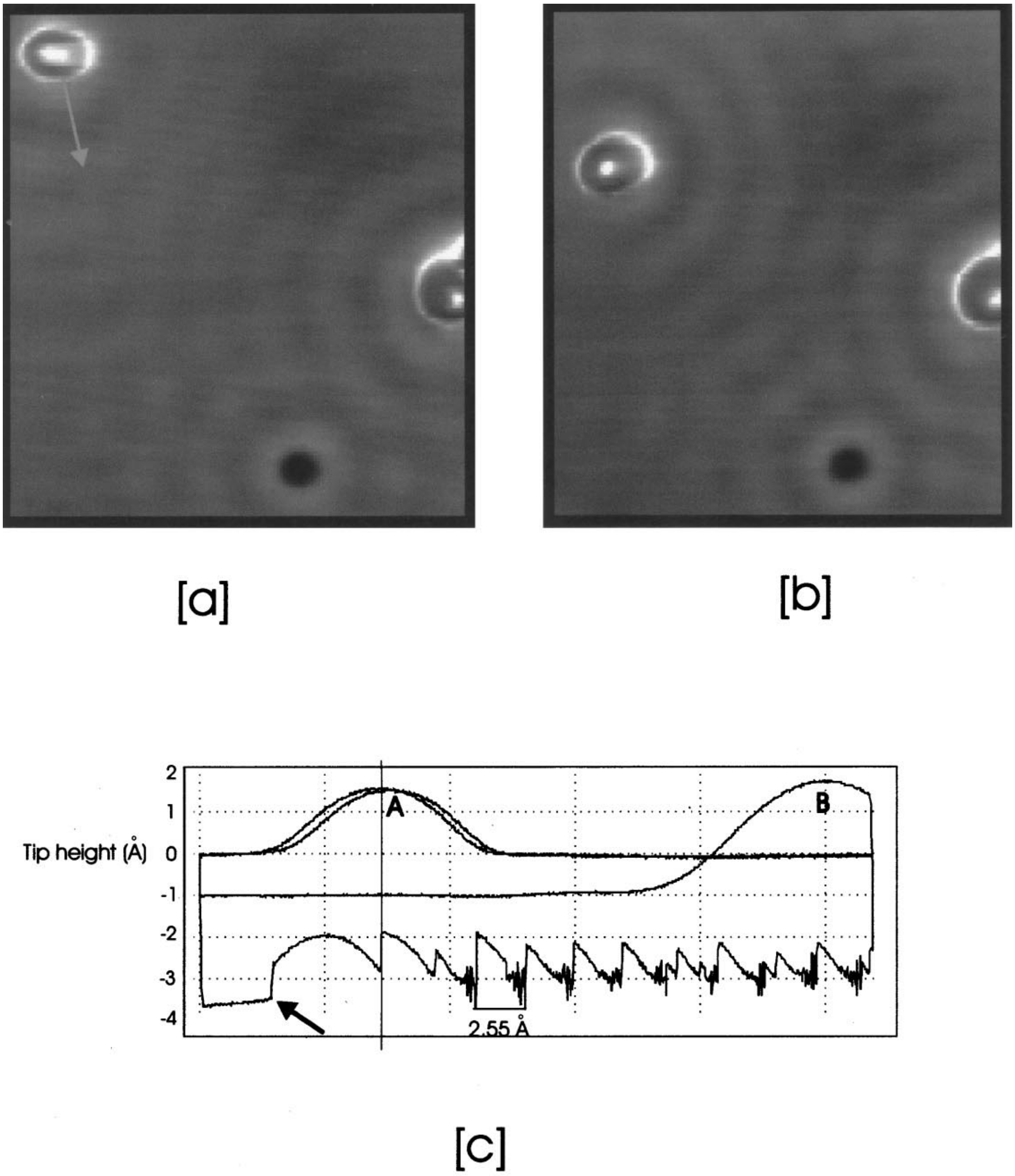

Fig. 2. An adsorbed diiodobenzene molecule at the upper left corner (a) is laterally moved to a lower position (b) on the Cu(111) surface. The black spot in the lower part of the image is an adsorbed CO molecule which is used as a landmark. The tip height curves during this operation are illustrated in (c), in which the tip first operates a trial movement along the manipulation path and records the initial molecule position (A), then the actual manipulation is performed by reducing the tip height by 3.5 Å from its original position. A sudden increase in tip height (shown by the arrow) occurs due to a jump of the molecule towards the tip. The vertical line is drawn to show the initial molecule position. The tip is retracted at the final position and rescanned along the manipulation path to access the success of the operation. During this, the final position of the molecule is recorded at B ($V_t = 300$ mV, $I_t = 1.3$ nA).

Most molecules adsorbed at the step edges are located at the lower terrace sites. The 1,4-diiodobenzene molecule constitutes of two iodine atoms attached at opposite ends of a benzene ring and they appear in elliptic shapes on the Cu(111) plane terrace (Fig. 2a); however, the detailed structure of the constituents of the adsorbed molecules could not be easily resolved in STM images.

Lateral manipulation of the molecules on the plane terraces can be performed along the close-packed rows, i.e., [110] directions. During the operation, the STM tip was first scanned over a path along which the molecule was to be moved. Actual manipulation was done by reducing the tip height when the tip approached to the molecule in order to increase the tip–molecule interaction. Then the tip was moved along the predetermined path in constant-current mode while the corresponding tip height curve was recorded. When the final destination was reached, the tip movement was terminated and the tip was retracted to its original height, i.e., further away from the molecule. This greatly reduced the tip–molecule interaction and the molecule remained in its final position. Completion of the task was confirmed by rescanning the tip backwards along the movement path. A typical example of such an operation is described in Fig. 2.

The diffusion dynamics of the molecule during the lateral manipulations can be understood from the corresponding tip height curves as shown in Fig. 2c. In this curve the molecule jumps towards the tip by one copper atomic site (2.55 Å) during approach of the tip from its initial position. This is caused by the attractive interaction between the tip and the molecule. After the tip passes over the molecule, which gives its contour line, the molecule follows the tip by performing a jump corresponding to the nearest-neighbour distance between copper atomic sites. Since the system is operating in constant-current mode, a sudden increase in the tip height occurs due to the feedback loop. The tip continues to move forward by following the molecule contour and again the molecule performs another jump, resulting in a saw-tooth-like behaviour. This tip height curve demonstrates typical 'pulling' mode behaviour in which the molecule follows the tip motion by means of discontinuous jumps. It can be easily realised from this curve that most of the jumps have the same distance of 2.55 Å, which is the nearest-neighbour (nn) distance of copper atoms along the [110] direction. Thus, the molecule has preferred adsorption sites.

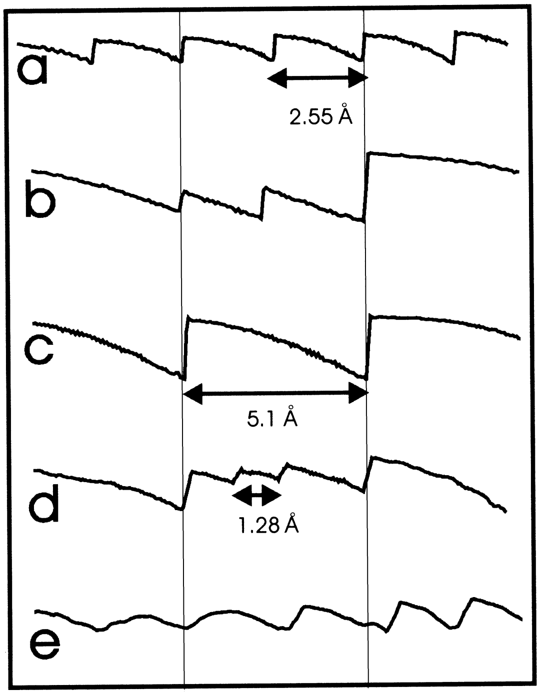

Fig. 3. Various tip height curves illustrating the artificial diffusion dynamics of a molecule along the close-packed row directions of Cu(111) during the lateral manipulation process: single copper-atomic-site hops (a), mixed single and double copper-atomic-site hops (b), double atomic hops (c), mixed 'hopscotch', single and double copper-atomic-site hops (d) and sliding and pulling (e).

Fig. 3 describes several different types of tip height curve for the lateral manipulation of diiodobenzene along the Cu(111) close-packed row directions. Normally, repeated hops with single copper atomic sites can be observed when tunnelling resistances between 95 kΩ and 1 MΩ are used. By increasing the tunnelling gap resistance during the operation, which eventually decreases the tip–molecule interaction force, hops with two copper atomic sites can be also induced. Fig. 3b illustrates mixed single and double copper-atomic-site hops of the molecule by increasing the tunnelling resis-

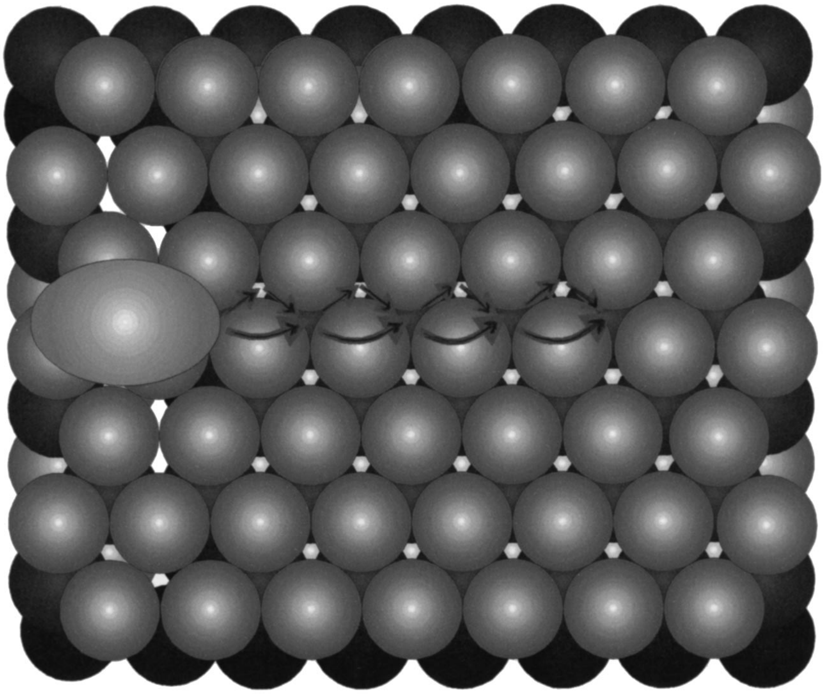

Fig. 4. Schematic drawing illustrating the possible diffusion paths of diiodobenzene along the Cu(111) close-packed rows. The curved arrows demonstrate the single copper-atomic-site hops in which the molecule will jump to only hexagonal close-packed (hcp) or face-centred cubic (fcc) sites. The zig-zag arrows demonstrate 'hop-scotch' motion in which the molecule will visit both fcc and hcp sites.

tance from 1 to 1.3 MΩ. At a tunnelling resistance of 1.4 MΩ, purely double copper-atomic-site hops can be observed (Fig. 3c). In this case, the in-plane component of the tip–molecule attractive force overcomes the hopping barrier of the molecule only when the tip is moved further down the molecule slope.

The preferred possible hopping sites of diiodobenzene on the Cu(111) surface are demonstrated in Fig. 4. The molecule prefers to jump either on fcc or hcp sites along the close-packed direction during the lateral movement, as shown with the curved arrows. However, if the tip is laterally shifted towards either to the left or right side of this path, then a 'hop-scotch' [12] type movement of the molecule can be observed as shown by the zig-zag arrows in Fig. 4. In this case, the molecule visits both hcp and fcc sites during its motion and the resulting tip height curve contains smaller jumps with 1.28 Å distance (Fig. 3d).

Attempts at controlled movement of the molecule along directions other than the close-packed rows were not successful: the molecule remained in its position. This highlights the preferred diffusion path of diiodobenzene on Cu(111) as being along the close-packed rows. In addition, since the diiodobenzene molecule has a relatively large size and contains more atoms than a CO molecule, it can easily fall apart during the lateral manipulation process. Thus, care must be taken during the manipulation operation.

Apart from the pulling mode, we can also induce sliding mode manipulation [7] of diiodobenzene if very low tunnelling resistance values (<90 kΩ) are used. Fig. 3e shows the sliding behaviour in the first part of the tip height curve. In this part, the molecule is trapped under the tip and both tip and molecule move smoothly together along the contour of the surface copper atoms. Later, the tip height curve changes to normal pulling behaviour, indicating that the molecule has escaped from such a trap.

In conclusion, we have shown here that relatively large molecules such as diiodobenzene can be laterally manipulated in a controlled manner at low temperatures. From the experiments we learned that the molecules have preferred diffusion paths during their movement on the Cu(111) surface; i.e., along the close-packed row directions. Even though the leading lateral manipulation mode is 'pulling', the 'sliding' mode manipulation could also be performed. By varying the tunnelling resistance, single- or double-site molecule hops can be induced at will. With this achievement, single-molecule engineering processes — such as the construction of molecular wires or molecular electronic devices, and even new man-made artificial molecules on crystal surfaces — get a step closer.

Acknowledgement

This work was supported in part by the DFG (RI 472/3-2 and SFB 290).

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