Manipulations of Individual Molecules by Scanning Probes

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ABSTRACT

In this letter, we suggest a new method of manipulating individual molecules with scanning probes using a "pick-up-and-put-down" mode. We demonstrate that the number of molecules picked up by the tip and deposited in a different location can be controlled by adjusting the pulling velocity of the tip and the distance of closest approach of the tip to the surface.

Introduction. Soon after the invention of scanning tunneling microscopy (STM) and atomic force microscopy (AFM), it was recognized that scanning can alter surface topography. At that time, this was considered to be a drawback for imaging. However, these observations led to the idea of controllable modifications of surface structure on the atomic scale, which attracted the attention of a large number of research groups.[1−4] The ability to manipulate individual atoms, molecules, and clusters with scanning probes has opened new fascinating areas of research and allowed us to perform "engineering" operations at the ultimate limits of fabrication.

Manipulations are usually classified into two types: lateral and vertical.[2−4] In the lateral case, an object is displaced (pulled, pushed, or slid) from one position to another on the surface, whereas in the vertical case the object is transferred between the surface and the tip. The vertical mode is also referred as "pick-up-and-put-down".[3] Lateral movements of adsorbates have been the subject of numerous experimental and theoretical studies.[5−9] However, controllable vertical manipulations of individual adsorbates by AFM and STM are in their early stages.[3,4,10−12] It is more difficult to control vertical manipulations than lateral ones because the energy barriers needed to be overcome when pulling an individual adsorbate off of a surface are usually higher than for lateral movements.

When a tip is brought into close proximity of a surface, the two potential wells, corresponding to the equilibrium position of the adsorbate on the tip or on the surface, when they are far apart, overlap (Figure 1). As a result, the barrier for the transfer of the adsorbate between the surface and the tip decreases. The remaining barrier can be crossed sponta-
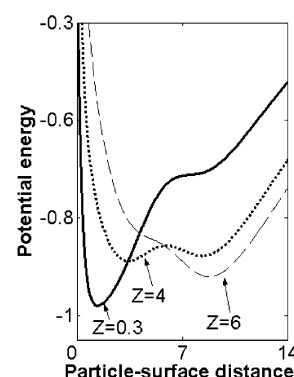

Figure 1. Schematic presentation of a typical evolution of the effective potential experienced by the molecule with an increase in the tip−surface distance. Parameter values: $U_0^{bulk}/U_0^{t-m} = 0.1$, $U_0^{surf}/U_0^{t-m} = 0.05$, $d/R_C^{t-m} = 2$, $l_Z/R_C^{t-m} = 6$. Lengths and energy are in units of R_C^{t-m} and U_0^{t-m}, respectively. Definitions of the parameters are given in the text.

neously because of the presence thermal fluctuations. However, because the involved relaxation times compete with the moving tip, the adsorbate cannot always follow the motion of the tip spontaneously, and the probability that the adsorbate transfers between the surface and the tip depends not only on the tip proximity but also on its velocity. In this letter, we demonstrate that the number of molecules picked up by the tip and deposited on another surface can be controlled by adjusting the pulling velocity of the tip and the distance of closest approach of the tip to the surface. This differs from an earlier suggestion of controlling the extraction of atoms from a surface through the duration of maximal approach and tip displacement toward the surface.[10]

Model. To mimic the manipulation of adsorbates by scanning probe microscopy, we introduce a model that consists of a monolayer of N interacting molecules with masses m and coordinates $r_i = \{x_i, y_i, z_i\}$ located on a

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substrate, a tip of mass M, and center-of-mass coordinate R_i = $\{X_i, Y_i, Z_i\}$. The tip is pulled by a spring of stiffness K in the z direction perpendicular to the surface $\{x, y\}$. The spring is connected to a stage that moves with a constant velocity V. The dynamics of this system is described by a system of $3N + 3$ equations of motion for the tip and the molecules:

$$M\frac{\partial^2 R}{\partial t^2} + \Gamma\frac{\partial R}{\partial t} + \sum_{i=1}^{N}\frac{\partial U^{t-m}(r_i - R)}{\partial R} + \frac{\partial U^{t-s}(R)}{\partial R} +$$

$$K(R - Vt) = 0 \quad (1)$$

$$m\frac{\partial^2 r_i}{\partial t^2} + \frac{\gamma \partial r_i}{\partial t} + \frac{\partial[U^{t-m}(r_i - R) + U^{m-s}(r_i)]}{\partial r_i} +$$

$$\sum_{i \neq j}^{N}\frac{\partial U^{m-m}(r_i - r_j)}{\partial r_j} = f_i(t) \qquad i = 1, ..., N \quad (2)$$

Here the potentials U^{m-m}, U^{m-s}, U^{t-m}, and U^{t-s} describe molecule−molecule, molecule−substrate, molecule−tip, and tip−substrate interactions, respectively. The parameters Γ and γ account for the dissipation of the kinetic energy of the tip and of each molecule, correspondingly. The effect of the thermal motion of the adsorbates is given in terms of a random force $f_i(t)$, which is δ-correlated, $\langle f_i(t)f_i(0)\rangle = 2m\gamma k_B T\delta(t)\delta_{ij}$. T is the temperature, and k_B is the Boltzmann constant. Our model assumes the classical limit based on macroscopic time scales involved in the manipulations.

In our numerical simulations, the molecule−molecule and tip−molecule interactions have been modeled by Morse potentials

$$U^{m-m}(r_i - r_j) =$$
$$U_0^{m-m}\left\{\left[1 - \exp\left(\frac{-2b^{m-m}(r_i - r_j - R_C^{m-m})}{R_C^{m-m}}\right)\right]^2 - 1\right\} \quad (3)$$

$$U^{t-m}(R - r_i) =$$
$$U_0^{t-m}\left\{\left[1 - \exp\left(\frac{-2b^{t-m}(R - r_i - R_C^{t-m})}{R_C^{t-m}}\right)\right]^2 - 1\right\} \quad (4)$$

whereas for U^{m-s} and U^{t-s} we used

$$U^{m-s} = \{U_0^{bulk} + U_0^{surf}[\cos(ax) + \cos(ay)]\}\exp\left[\frac{-(z - l_z)^2}{d^2}\right] \quad (5)$$

$$U^{t-s} = C_0 \exp\left[\frac{-(Z - L_z)^2}{c_0^2}\right] \quad (6)$$

where U_0^{t-m}, b^{t-m}, R_C^{t-m}, U_0^{m-m}, b^{m-m}, and R_C^{m-m} are the parameters of the Morse potentials. It was also taken into account that the dissipation γ decreases when the molecules move away from the surface: $\gamma(z) = \gamma_0[1 + \exp(-z^2/d^2)]$. It should be emphasized that our conclusions are mostly independent of the particular forms of the potentials U^{t-m}, U^{m-s}, U^{m-m}, and U^{t-s}.
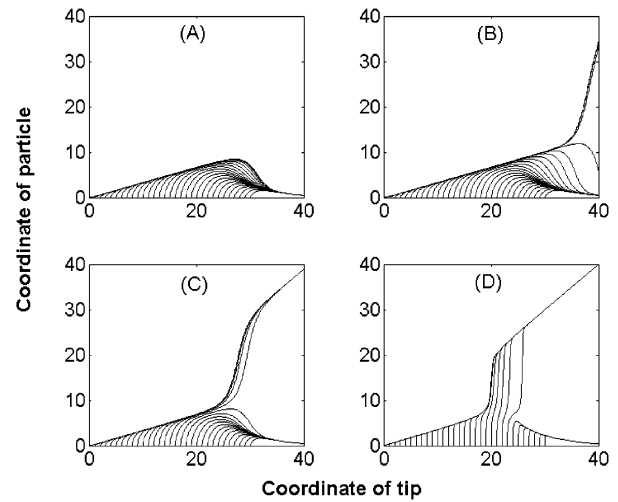
Figure 2. Trajectories of atoms as a function of the tip coordinates for four values of the pulling velocity V: (A) 10, (B) 9.5, (C) 7.5, (D) 0.7. Parameter values: $U_0^{bulk}/U_0^{t-m} = 1.9$, $d/R_C^{t-m} = 10$. Lengths and velocities are in units of R_C^{t-m} and $\gamma_0 R_C^{t-m}/m$, respectively.

Qualitative Considerations of Nanomanipulation. Qualitative features of the suggested mechanism of the manipulation of individual molecules can be understood within the framework of a simplified 1D model. The model describes a single particle located on the uniform surface and interacting with the tip, which is pulled off the surface with a constant velocity of $V = Z = $ const, starting from a height of Z_0. Equations 1 and 2 reduce to a 1D equation of motion for the position of the molecule, z, which under overdamped conditions ($\gamma \gg 1$) reads

$$\frac{dz}{dZ} = -\frac{\partial U_{eff}/\partial z}{\gamma V} \quad (7)$$

Here $U_{eff} = U^{m-t}(z, Z) + U^{m-s}(z)$ is an effective potential experienced by the molecule due to the surface and the tip. The coordinate Z of the tip enters as a parameter.

The typical evolution of the potential U_{eff} with an increase in the tip−surface distance Z is shown schematically in Figure 1. When the tip and the surface are in close contact, the two wells corresponding to adsorption on the tip or on the surface overlap, and the resulting U_{eff} can attain the form of an asymmetric single well. With an increase in the tip−surface distance, the effective potential U_{eff} takes the form of a two-well potential, and the barrier between two minima grows.

The set of solutions of eq 7 for different values of starting height Z_0 and velocity V presents trajectories in the coordinates (z, Z), which give a phase portrait of the dynamical system. Typical phase portraits are shown in Figure 2 for four values of pulling velocities V. All trajectories in Figure 2 can be separated into two types: (1) trajectories that correspond to a regime where the molecule remains on the surface and (2) trajectories that belong to a regime in which the tip picks up the molecule and drives it away from the surface. For the first type of trajectory, $z \rightarrow z_{ad}^s$ when $Z \rightarrow$

∞, and for the second type of trajectory, $z \to Z - z_{ad}^t$ when $Z \to \infty$, where z_{ad}^s and z_{ad}^t are the molecule−surface and molecule−tip distances for the cases of equilibrium adsorption at the substrate (in the absence of the tip) and at the tip (in the absence of the substrate). Figure 2 shows that even by being trapped by the tip at small Z the molecule cannot always follow the tip motion. Because of a finite relaxation time $1/\gamma$, this depends on the tip velocity V. For high pulling velocities, the molecule always remains at the surface, independent of the starting tip position Z_0 (Figure 2a). As V decreases, the second type of solution set is seen in Figure 2b−d. Furthermore, the starting position of the tip, Z_0, for which the molecule can still be picked up by the tip increases with a decrease in the pulling velocity.

The above consideration allows us to define the Z_0-dependent critical velocity of the tip, $V_{cr}(Z_0)$, that is the maximal V for which the tip drives the particle away from the surface. The result is presented in Figure 3. For all values of V and Z_0 lying below the curve $V_{cr}(Z_0)$, the tip does pick up the molecule, and for the values above the curve, the molecule does not follow the tip but remains on the surface.

The largest allowed value of the critical velocity can be estimated analytically. To do this, we consider the motion of the molecule that is trapped by the tip and assume that the distance between the molecule and the tip remains constant, $z_* = Vt - z(t) = \text{const}$, when the tip is driven away from the surface. In this regime, an effective potential experienced by the molecule is dominated by the attraction to the tip, and it can be approximated by $U_{eff} \approx \tilde{\epsilon} \exp[-(z - Vt)^2/\tilde{\sigma}^2]$. Under these conditions, the equation of motion (eq 7) leads to the following relation between z_* and V:

$$1 - \left(\frac{\tilde{\epsilon}}{\gamma V}\right) z_* \exp\left(-\frac{z_*^2}{\tilde{\sigma}^2}\right) = 0 \qquad (8)$$

Equation 8 has a solution only for $z_* < \tilde{\sigma}/\sqrt{2}$ and $V < V_{cr}^* = \tilde{\epsilon}\tilde{\sigma}/(\gamma\sqrt{2e})$. For $V > V_{cr}^*$, the molecule cannot follow the tip motion and remains on the surface. Thus, $V = V_{cr}^*$ is the maximal driving velocity for which the tip can pick up the molecule. The estimated value of V_{cr}^* is in good agreement with the numerical results presented in Figure 3.

The dependence of the critical velocity on Z_0, $V_{cr}(Z_0)$, does not only give a clue on how to manipulate single molecules but also allows us to estimate the range of tip velocities for which the tip picks up a desirable number, N_{tr}, of molecules when it is driven away, starting at the distance $Z = Z_0$. To do this, we define a function $Z_{cr}(V)$ that gives the maximal value of the initial tip−surface distance for which the tip can trap the molecule, being driven away with a velocity V. The function $Z_{cr}(V)$ is the reciprocal of the function $V_{cr}(Z_0)$. Using this information, we conclude that the tip will pick up all molecules located under the tip within a circle of radius $R = \sqrt{Z_{cr}^2(V) - Z_0^2}$ (Figure 4). Here we assumed that molecules are distributed uniformly on the surface and do not interact among themselves. Taking into account that $R \propto \delta\sqrt{N_{tr}}$, where δ is the average distance between adsor-
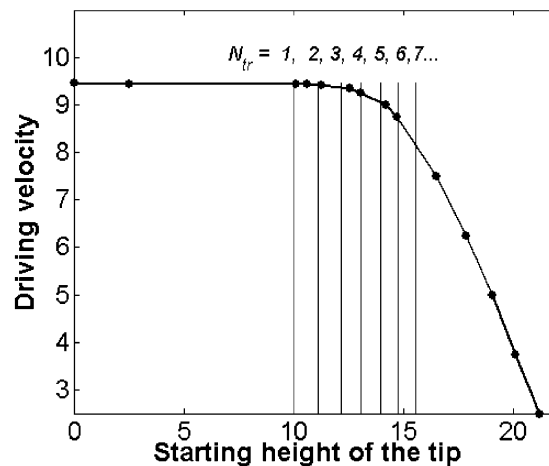

Figure 3. Maximal velocity for which the tip still drives a particle away vs starting height of the tip. For all values V and Z_0 below the curve $V_{cr}(Z_0)$, the tip picks the molecule up, whereas for the values above the curve the molecule remains on the surface. Intersections of the curve $V_{cr}(Z_0)$ with vertical lines give the maximal tip velocity for which the tip picks up a given number of particles, $N_{tr} = 1, 2,...,7$, when driven from stating height Z_0. Parameter values are the same as those in Figure 2.
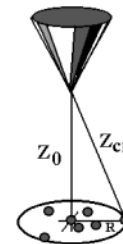

Figure 4. Schematic explanation of the analytical estimation of the critical velocity V_{cr}: the tip picks up all of the molecules located under the tip within a circle of radius R.

bates on the surface and N_{tr} is the number of molecules located within the circle, we obtain the following relation between the pulling velocity and the number of molecules picked up by the tip:

$$Z_{cr}(V) = \sqrt{Z_0^2 + \delta^2 N_{tr}} \qquad (9)$$

Thus, intersections of the curve $V_{cr}(Z_0)$ with vertical lines $Z = \sqrt{Z_0^2 + \delta^2 N_{tr}}$ for $N_{tr} = 1, 2, 3...$ that are shown in Figure 3 give the maximal tip velocity for which the tip picks up a given number of particles, N_{tr}, when it is driven away from the surface starting at distance Z_0.

It should be noted that the range of tip velocities suitable for controllable molecular manipulation strongly depends on the interaction of the tip with the molecules. The latter can be made adjustable by modifying the tip chemically.[13] In this way, the critical velocity can be moved into the desired range. Surprisingly, the characteristic time to extract a molecule has been found to be as short as 10 ms,[10] a time that allows the tip velocity to act as a control parameter.

The same mechanism of manipulation by adjusting the tip velocity and the distance of the closest approach to the

surface can be used for the deposition of a given number of molecules on the surface. Below, we illustrate the proposed mechanism of the pick-up-and-put-down mode of manipulation by numerical simulations.

Results of the Simulation and Discussion. We have performed numerical simulations of eqs 1 and 2 that describe the coupled dynamics of the externally driven tip and the monolayer of adsorbed molecules. In solving the equations, we started from the equilibrium configuration produced when the tip is brought into close contact with the surface. Then the tip was pulled away from the surface by a spring with a constant velocity. The number of molecules picked up by the tip has been found repeatedly. As a result, we obtained a map of the probability of trapping a given number of particles by the tip at a given driving velocity, which is presented in Figure 5. Regions of high and low probability are displayed by red and blue, correspondingly. Figure 5b presents the distribution functions of the number of trapped particles for three representative velocities. The map shows that the number of molecules picked up by the AFM tip can vary over a wide range; for the parameters used here, this number varies from 0 to 8. The number one can be achieved by tuning the driving velocity. In accordance with the qualitative picture discussed above, the number of trapped molecules decreases with increasing driving velocity.

It should be noted that not all possible numbers of molecules can be trapped with equal probability. The probability map demonstrates that there are "preferred" numbers of molecules: 1, 3, 5, and 8, which can be picked

Figure 6. Examples of preferred configurations formed by the molecules around the tip: (A) five particles (four in a plane and the fifth atop the tip) and (B) eight particles (six form a hexagonal structure with the tip in the center and the other two are out of the plane).

up with a high probably, whereas trapping 4, 6, and 7 molecules is less probable. The origin of such "magic numbers" can be explained by analyzing molecular configurations that can be formed around the tip. Figure 6 presents examples of the energetically preferred configurations that have been observed in the simulations: five particles (four in a plane and the fifth atop the tip, Figure 6a) and eight particles (six form a hexagonal structure with the tip in the center and two others are out of the plane, Figure 6b). We remark that the shape of these configurations and the number of particles in them are not universal. They are determined by the radius of the tip and parameters such as molecule−tip and molecule−molecule interactions.

The map shows that changing the pulling velocity indeed allows one to control the number of molecules transferred from the adsorbed layer to the tip. The proposed manipulation can be optimized and further controlled by adjusting the distance of the closed approach of the tip to the surface and waiting a certain length of time before the pulling out of the surface.
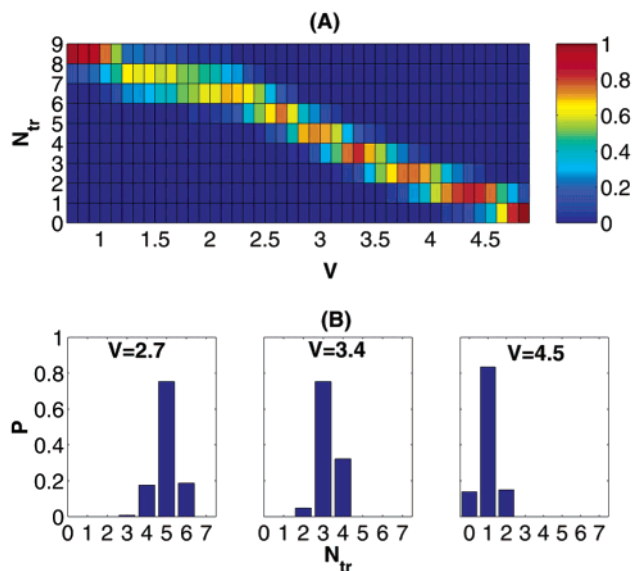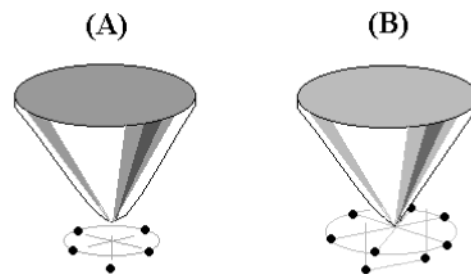
Figure 5. (A) Probability map giving the probability of trapping a given number of particles at a given driving velocity of the tip. The bar to the right of the map sets up the correspondence between the colors and the probability $P(N_{tr}, V)$. (B) Histograms for the number of trapped particles corresponding to three values of velocity. Parameter values: $N = 100$, $M = 30m$, $\Gamma = 30\gamma_0$, $a/R_C^{t-m} = 6.3$, $l_Z/R_C^{t-m} = 2$, $d/R_C^{t-m} = 1$, $KR_C^{t-m}/U_0^{t-m} = 4.7$, $U_0^{m-m}/U_0^{t-m} = 0.07$, $b^{m-m} = 0.6$, $R_C^{m-m}/R_C^{t-m} = 1$, $U_0^{bulk}/U_0^{t-m} = 0.7$, $U_0^{surf}/U_0^{t-m} = 0.05$, $C_0/U_0^{t-m} = -0.8$, $c_0/R_C^{t-m} = 2$, $L_Z/R_C^{t-m} = -2$, $k_B T/U_0^{t-m} = 10^{-3}$. Lengths and velocities are in units of R_C^{t-m} and $\gamma_0 R_C^{t-m}/m$, respectively.

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