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Quantum atom switch: Tunneling of Xe atoms

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Recently Eigler, Lutz, and Rudge [Nature **352**, 600 (1991)] have reported a bistable switch that derives its function from the motion of a single Xe atom. It has been shown that this atom can be transferred, in a reversible way, from a scanning-tunneling-microscope tip to a sample by means of a voltage pulse. In this paper we show that the atom transfer process can be understood in terms of a single-atom-tunneling process, while a mechanism similar to the heating-assisted electromigration cannot account for the experimental observations. We find that there is a nonzero probability of atom transfer even at zero applied voltage, i.e., the transfer rate cannot follow a power-law dependence with the applied pulse at small voltages. We present a tunneling model, based on the charge transfer from the metal to the $6s$ resonance of the Xe atoms, which is consistent with the available experimental data.

The most dramatic evidence of the scanning-tunneling microscope's (STM) ability to manipulate individual atoms has been presented recently by Eigler, Lutz, and Rudge.[1] They have been able to transfer a single Xe atom back and forth between a STM tungsten tip and a nickel substrate surface by means of a voltage pulse. As the conductance of a tunnel junction depends exponentially on the spacing between electrodes, even a slight rearrangement of the atom leads to a measured change in the STM conductance. Their device switches between a low conductance state when the atom is on the substrate to a high conductance state when the atom is on the tip.

The physical mechanism that causes the motion of the atom in the "atom switch" is not clear. Any candidate mechanism should explain, at least, the qualitative behavior observed in the experiment. This behavior is resumed in the following items.

The motion of the xenon atom is always towards the positively biased electrode.

The atom switch is only effective in a small window of tip-sample distances such that the junction resistance is between 0.7 and 1.5 MΩ. At smaller separations (resistances) the xenon atom moves spontaneously to the tip without the need to apply a positive voltage pulse. At larger separations the xenon atom sometimes escapes from the junction region entirely.

The transfer rate of a xenon atom from the surface to the STM tip seems to have a power-law dependence with the current during the applied voltage pulse.

Several mechanisms for atom transfer, such as ionization or negative-ion formation followed by field evaporation, have been discussed. However, none of them can account for all the observed phenomena. It was speculated[1] that heating-assisted electromigration[2,3] could be a good candidate. Electromigration is odd in the applied field, and the competition between electron heating and the relaxation of vibrational energy to the lattice could account for the observed transfer rate.

None of the proposed mechanisms include two physical aspects of the problem that must play an important role in the understanding of the switching mechanism. The first aspect is related to the nonzero probability of quantum tunneling of the atom between tip and sample. The second is related to the charge transfer from the metal to the $6s$ resonance of the Xe atom.[4,5(a)] In this paper we propose a switch mechanism which is based mainly on these two physical facts. At first sight it seems strange to talk about tunneling of such a "big" object mainly if one is used to thinking about tunneling of electrons through barriers with typical widths of angstroms or tens of angstroms. However, this is not so remarkable as soon as one remembers that the characteristic tunneling parameters are inversely proportional to the square root of the mass of the tunneling entity. Then Xe atoms, like electrons, can tunnel provided that the energy barriers and tunneling lengths are small enough. As we will see, this mechanism is consistent with all the experimental observations.

Let us first analyze qualitatively the origin of the small window of tip-sample distances in which the atom switch is effective. Experimental switching occurs for tip-sample resistances, R, between $R_{\min} \approx 0.7$ MΩ and $R_{\max} \approx 1.5$ MΩ. Let Y be the lateral separation between the tip and the Xe atom and $s(Y)$ the tip-sample distance. Then, from the experimental STM results and atom-on-jellium calculations,[5(a),6] $R_{\min}$ and $R_{\max}$ correspond to tip-sample distances $s_{\min}(Y=\infty) \approx 5.3$ and $s_{\max}(Y=\infty) \approx 5.7$ Å. Taking into account the normal tip displacement when the tip is just on top of the Xe atom, we estimate[7] $s_{\min}(Y=0) \approx 7.1$ and $s_{\max}(Y=0) \approx 7.5$. Now, in the switching regime, the tip is left at a fixed position above and ≈ 5 Å to the side of the Xe atom. Let D be the distance between the tip and sample surfaces at the position of the Xe atom. Although the exact value of D depends on the geometry of the tip surface, it should be of the order of $s(Y=0)$. Below $D = D_{\min}$ the Xe atom jumps spontaneously from the sample to the tip even without any applied pulse.

On the other hand, for distances larger than D_{max}, the xenon atom, after an applied pulse, instead of jumping to the tip, diffuses over the Ni surface indicating that the diffusion barrier on the surface is lower than the barrier towards the tip. It is then possible to have an idea of the order of magnitude of the parameters involved in the atom switch. In the switching range, the xenon atom sees a potential barrier ΔE lower than the diffusion barrier on the surface [typically $\Delta E \approx 40$ meV (Ref. 8)] but large enough to avoid spontaneous jump. On the other hand, the equilibrium distance of xenon above the surface, Z_e, is ≈ 2.65 Å with respect to the surface jellium edge.[9] Then, at tip-sample distances of the order of 7 Å, the Xe atom jumps a distance of the order of or smaller than 1.5 Å. Such small barriers and distances strongly suggest the possibility of atom tunneling between the tip and sample.

In order to have a quantitative comparison with the experiments we have developed a theoretical model of the atom switch. As a first step, the model involves an estimation of the interaction potential, $U(Z)$, between the xenon atom and the Ni and W surfaces. At large separation distances, Z, between a xenon atom and a surface, $U(Z)$ is essentially a van der Waals interaction $\approx C(Z - Z_0)^{-3}$, with C being typically of the order of ≈ 3.3 eV Å^3.[10] Close to the equilibrium position, the interaction is no longer van der Waals. We assume a Morse-like potential with a potential well V_0 taken from the experimental results on the adsorption energy: $V_0\{\text{Xe/Ni}\} \approx 0.24$ eV (Ref. 11) and $V_0\{\text{Xe/W}\} \approx 0.35$ eV.[12] Assuming that these two different behaviors join smoothly at the Morse inflexion point, we have

$$U_{\text{Xe/surface}}(Z) = \begin{cases} V_0(e^{-2(Z-Z_e)/b} - 2e^{-(Z-Z_e)/b}) & \text{if } Z - Z_e < b\ln 2 \\ C(Z - Z_0)^{-3} & \text{otherwise,} \end{cases} \quad (1)$$

where Z_e is the equilibrium distance, $Z_0 = -3.8b$ is the van der Waals reference plane, and $b^3 = 0.015C/V_0$ (distances are given in Å and energies in eV). The total interaction potential, U_T, of a xenon atom between the tip and sample surfaces separated at a distance D would then be $U_T(Z) = U_{\text{Xe/Ni}}(Z) + U_{\text{Xe/W}}(D - Z)$. The resulting double-well potential is sketched in Fig. 1.

When the xenon atom is, for example, on the Ni surface it has to surmount an energy barrier ΔE in order to jump to the tip (see Fig. 1). In Fig. 2 we show the energy barrier as a function of the tip-sample distance D. Even in the absence of applied voltage, there is a probability of atom transferring per unit time. Assuming thermal assisted quantum tunneling, a typical transfer rate, τ^{-1}, would be

$$\tau^{-1} \approx \left\{\sum_{i=0} w_i e^{-E_i/K_BT} T(E_i)\right\} \left\{\sum_{i=0} e^{-E_i/K_BT}\right\}^{-1}, \quad (2)$$

where w_i and E_i are the frequencies and energies of a

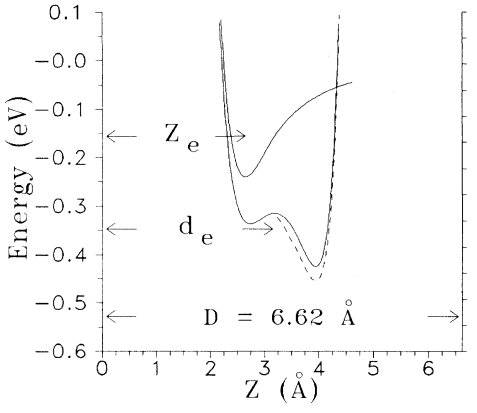

FIG. 1. Potential energy diagram for a xenon atom placed between a Ni surface ($Z = 0$) and a W tip ($Z = 6.62$ Å). Distances are referred to the jellium edges. The single-well potential represents the Xe-Ni surface interaction in the absence of the tip. Z_e is the xenon-surface equilibrium distance. d_e is the effective image plane on the adsorbed atom. The dashed line is the potential energy with the tip biased at +0.1 V with respect to the surface.

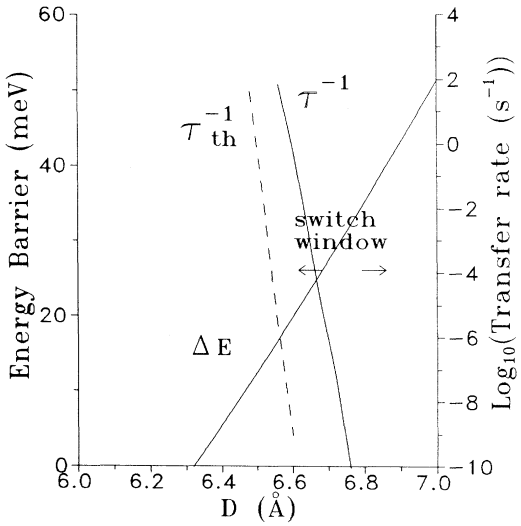

FIG. 2. Atom energy barrier, ΔE, as a function of tip-sample separation D (left scale) and calculated transfer rates for atom tunneling and pure thermal excitation (continuous and dotted line, respectively; right scale) as a function of the tip-sample distance for zero applied voltage. The adsorbed atom remains stable on the Ni surface for distances larger than ≈ 6.6 Å. For distances larger than ≈ 6.8 Å the energy barrier becomes larger than the barrier for diffusion over the surface. The estimated theoretical window of distances in which the atom switch is possible is also shown.

xenon atom on the Ni well, $\exp(-E_i/K_BT)$ the occupation probabilities, and $T(E_i)$ the tunneling probabilities to go through the barrier. We have calculated τ^{-1} within the Wentzel-Kramers-Brillouin-Jeffreys (WKBJ) approximation.[13] Notice that the use of the WKBJ approximation is justified since the atom wavelength is much smaller than the width of the barrier and the tunneling probabilities are extremely small.

The calculated transfer rates of a xenon atom from the Ni surface to the STM tip at zero applied voltage are shown in Fig. 2 as a function of the tip-sample distance. As can be seen, in the absence of applied voltage, the xenon atom will be stable on the Ni surface until tip-sample distances, D, at which the transfer rate goes above, say, 10^{-1} s^{-1}, i.e., D of the order of 6.6 Å. Below this distance, the Xe atom would *tunnel* spontaneously to the tip. Since the well depth on the tungsten tip is larger than on the Ni surface, the energy of the xenon atom is released rapidly (typically in $\approx 10^{-10}$ s) and the atom remains stable on the tip surface. Above ≈ 6.8 Å ΔE is larger than 40 meV, and the xenon atom could diffuse over the surface instead of jump towards the tip. These results are in close agreement with the estimated experimental switch window discussed above. In Fig. 2 we have also plotted the calculated thermal rate, $\tau_{\rm th}^{-1}$, at 4 K without including atom tunneling. It is clear that at 4 K tunneling rates are much higher (about six orders of magnitude) than the thermal rates.

We now turn to the intriguing question of the origin of the switch dependence with the sign of the applied voltage pulse. This is related to the charge transfer from the metal surface to the xenon atom ("s-resonance model"[4]). Because of the $6s$ resonance, the conduction electrons at the Fermi level protrude further out into the vacuum at an adsorbed Xe atom than over the bare metal.[4,5] This effect leads to a simple physical picture of the charge distribution in the adsorbed atom. First, there is a charge transfer (or polarization) of the Xe electrons, close to the metal surface, towards the metal leading to the well-known Xe dipole moment. However, this charge is screened by the external field because it is closer to the metal surface than the image plane. On the other hand, in the $6s$ resonance there is some extra "negative" charge coming from the metal at a relatively large distance from the metal surface. Because of this extra charge, when the Xe atom is on the substrate surface, a negative voltage pulse, V, applied to the surface would introduce a perturbation, $\Delta U(Z)$, in the atom potential, leading to a lower barrier and, as a consequence, to lower transfer rates.

We can get an idea of the effect of the perturbation on the transfer rates by assuming a simple model. When the tip is over the xenon atom, the applied potential drops between the tip image plane and some effective image plane in the xenon atom at a distance $d_e \approx 3.15$ Å from the jellium edge.[14] It is likely that, because of the screening, the effect of the applied potential on the adsorbed atom is small. However, as we move the xenon atom towards the tip, the screening of the applied potential would be less effective, resulting in a net force. As a simple approximation, we will assume a linear perturbation potential between the effective image planes, i.e., between $Z = d_e$ when the atom is on the surface and $Z = D - d_e$ when it is on the tip,

$$\Delta U(Z) \approx -Q_{\rm eff} V \begin{cases} 0 & \text{if } Z < d_e \\ (Z - d_e)/(D - 2d_e) & \text{if } d_e < Z < D - d_e \\ 1 & \text{if } Z > D - d_e, \end{cases} \tag{3}$$

where $Q_{\rm eff}$ is the effective xenon charge and V the applied voltage. We estimated $Q_{\rm eff} \approx 0.1e$ from Ref. 5. We have calculated Eq. (2), for a fixed distance and $T = 4$ K, as a function of the applied voltage, for a xenon atom going from the Ni surface to the STM W tip. In Fig. 3 we present our results for $\log_{10}(\tau^{-1})$ as a function of the applied pulse, V, for a distance $D = 6.62$ Å (curve a). The transfer rate behavior is related to the tunneling probability dependence with the applied voltage. For small voltages ($Q_{\rm eff}V$ small), since the barrier height decreases linearly with the applied voltage, the tunneling transfer rates follow an approximately exponential-law dependence ($\log_{10}\tau^{-1} \propto V$) with the applied voltage. However, as $Q_{\rm eff}V$ increases there is a saturation effect on the transfer rate. This can be seen clearly if we assume larger values of the effective charge as in curve b ($Q_{\rm eff} = 0.3e$). This saturation effect appears as a consequence of the screening of the potential at the effective image plane d_e [see Eq. (3)]. Since the equilibrium position of the xenon atom, Z_e, is closer to the substrate surface than d_e, there is a remaining barrier even for larger voltages. This is shown in Fig. 1, where we have plotted the potential energy for $Q_{\rm eff}V = 30$ meV. Then, as the voltage increases there is a crossover from exponential to field-emission-like behavior ($\log_{10}\tau^{-1} \propto 1/V$),[15] similar to the well-known crossover from tunneling to field emission in tunnel junctions.

It is interesting to compare this transfer rate behavior, obtained with our "tunneling s-resonance" model, with other possible mechanisms. It has been suggested that the mechanism responsible for the experimental behavior could be similar to the heating-assisted electromigration at low temperatures. Following Ralls, Ralph, and Buhrman,[2] this could imply the existence of an effective atom temperature T_a which is different from the overall sample temperature T, and increases with the square of the applied voltage, i.e., $T_a \approx T + C \times V^2$. We have replaced T with T_a in Eq. (2) and calculated the corresponding thermal transfer rates for different values of the constant C. The results for $C = 0$ (no voltage dependence), 250 and 500 K V^{-2} are shown in Fig. 3 (curves c, d, and e). The behavior is quite different

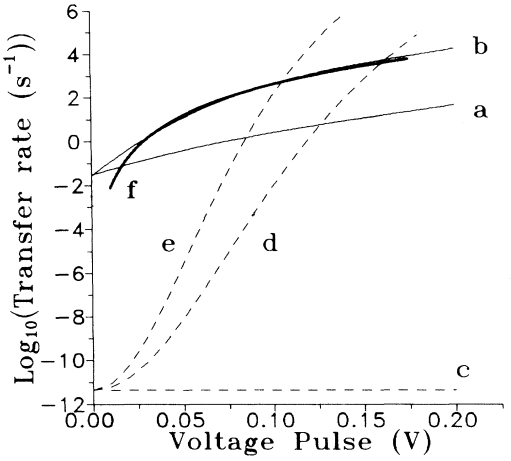

FIG. 3. Calculated transfer rate of a xenon atom from the Ni surface to the STM W tip as a function of the voltage pulse for a distance $D = 6.62$ Å. Continuous lines represent the results of our tunneling s-resonance model for two different effective charges $Q_{\text{eff}} = 0.1e$ (a) and $0.3e$ (b). Dashed lines are the results assuming an effective atom temperature $T_a = T + CV^2$ based on the thermal-electromigration model of Ref. 2. (Curve c is for $C = 0$, d for $C = 250$, and e for $C = 500$ K V^{-2}.) The power-law fit of the experimental results is also shown (thick line f).

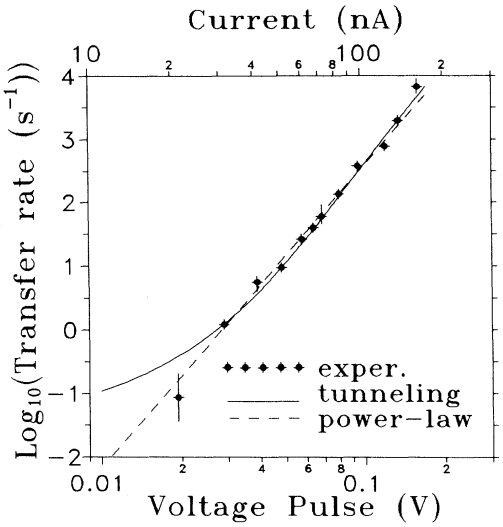

FIG. 4. Calculated transfer rate of a xenon atom from the Ni surface to the STM W tip as a function of the voltage pulse (with $D = 6.62$ Å, $Q_{\text{eff}} = 0.3e$; the same as curve b in Fig. 3). The experimental results obtained by Eigler, Lutz, and Rudge (Ref. 1) as well as their power-law fit ($\tau^{-1} \propto V^{4.9}$) are also shown. A quantum tunneling mechanism is consistent with the experimental behavior.

from that obtained with our model. These curves are orders of magnitude smaller than the corresponding tunneling s-resonance results and they meet only at temperatures higher than 10 K. In Fig. 3, the thick line represents the experimental fit with the power-law dependence ($\tau^{-1} \propto V^{4.9}$) proposed by Eigler, Lutz, and Rudge.

Although our model is able to reproduce qualitatively all the experimental observations, we could not get quantitative agreement unless we assume $D \approx 6.62$ Å and an effective charge, $Q_{\text{eff}} \approx 0.3e$. It is not clear whether this large effective charge has a physical origin or is an overestimation of our model. An increase of the effective charge could arise from different reasons. Lang's calculations of Xe adsorbed on a jellium surface[5(a),9] (leading to $Q_{\text{eff}} \approx 0.1e$) do not include tip-induced effects that could modify the width of the $6s$ resonance. On the other hand, dynamical screening effects can increase the effective charge as has been discussed in the analysis of the direct-force contribution in electromigration.[3,16] In Fig. 4, we represent our results together with the experimental results[1] corresponding to a fixed resistance $R \approx 0.9$ MΩ. The original fit with a power-law dependence is also shown in Fig. 4. As can be seen, the agreement between our results and the experiments is as good as that obtained with the power-law fit (of unknown physical origin), except for the experimental point (which has the largest error bar) at low voltage, $V \approx 0.02$ V. An interesting point is that the negative tip bias, $V \approx -0.02$ V (used to control the tip-sample distance) stabilizes the xenon atom on the substrate surface. In any case, the nonzero probability of atom tunneling at zero voltage implies that the power law cannot be valid at small voltages. It would then be possible to measure the transfer rates for very small, and even negative, voltages. More experiments in the low voltage region will clarify the situation.

Our model predicts an asymmetry of the transfer rates when the atom jumps from the W tip to the Ni surface. Because of the different adsorption energies, larger voltages are needed to transfer the Xe atom from the tip to the sample. As a consequence, there is a minimun voltage, V_{min}, below which reversible switching is not possible. Within our model, this minimun value is at least of the order of 0.3 V. However, for large fields, Eq. (3) is not a good approximation since it assumes a perfect screening of the field by the xenon atom and a better estimation of the field effect is needed.

We have shown that the physics of the "atom switch" can be understood in terms of a single-atom-tunneling process, while a mechanism similar to the heating-assisted electromigration cannot account for the experimental observations. The switch dependence on the sign of the applied pulse is associated to the charge transfer from the metal surface to the adsorbed xenon atom. Under the applied pulse, the atom "tunnels" through the potential barrier existing between the two electrodes. We have presented a simple model which is in good agreement with the available experimental data. It is worth noticing that the charge transfer to the $6s$ resonance of the adsorbed Xe atom depends on the substrate work function[4] (the charge increases as the work function decreases). This could be the reason for the larger conductance when the Xe atom is on the tip since the work function of a (110) Ni surface (≈ 5 eV) is larger than that of most of the W surface orientations (≈ 4.5 eV).

Although the quantitative agreement of our model with the experiments cannot be considered, strictly

speaking, as an evidence of the tunneling process, at least we have established it as a plausible mechanism that merits further experimental and theoretical investigation. However, we would like to emphasize that Xe atoms, like electrons, are quantum entities that are able to tunnel through potential barriers. Then, from a general point of view, because of the tunneling process there is always a finite probability of atom transfer, even at zero voltage, and the transfer rates cannot follow a power-law dependence with the applied pulse at small voltages.

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