

Imaging Xe with a Low-Temperature Scanning Tunneling Microscope

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We have obtained images of individual Xe atoms adsorbed on a Ni(110) surface using a low-temperature scanning tunneling microscope (STM). The atom-on-jellium model has been used to calculate the apparent height of a Xe atom as imaged with the STM and the result is found to be in good agreement with experiment. We conclude that the Xe $6s$ resonance, although lying close to the vacuum level, is the origin of the Fermi-level local state density which renders Xe "visible" in the STM.

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Scanning tunneling microscopes (STMs) have been used to image a wide variety of adsorbate atoms and molecules on both metal and semiconductor surfaces. Currently, the generally accepted view is that the theory of Tersoff and Hamann¹ provides an adequate description of the origin of contrast in STM images. In this theory it is shown that for small bias and constant current an STM image corresponds to a map of constant local state density at the Fermi level. The extent to which an adsorbate will be "visible" to the STM depends on how it locally changes this state density. Lang^{2,3} has shown that for single-atom adsorbates on metal surfaces, the crucial parameters in determining the apparent height of the atom in a low-bias STM image are the s -state and p -state densities due to the adsorbate at the Fermi level. Now Xe, as with the other rare-gas atoms, when adsorbed on a metal surface makes virtually no contribution to the state density at the Fermi level. It was therefore somewhat surprising to find that Xe is readily visible in the STM.

Here we discuss how we have obtained STM images of individual Xe atoms adsorbed on a Ni(110) surface. The ability to study the model system of a rare-gas atom adsorbed on a metal surface allows us to make a quantitative comparison of the theory of Lang^{2,3} with experiment. We find good agreement between theory and experiment. The $6s$ resonance⁴ of Xe, although lying near the vacuum level and therefore essentially unfilled, is found to be the source of the Fermi-level local state density by which Xe is imaged. Our results demonstrate that even though an atomic resonance of an adsorbate atom lies far above the Fermi level, it may nevertheless make the dominant contribution to an STM image if the size of the orbital associated with that resonance is such that it extends considerably further out into the vacuum than the bare-surface wave functions.

There exists a small body of evidence by which one might have estimated, prior to the present work,⁵ that Xe would be readily visible in the STM. Eigler and Schultz have measured the conduction-electron-spin

scattering cross sections of rare-gas atoms on a metal surface.⁶ They interpreted their results as indicating that the Fermi-level conduction-electron density builds up in the core of an adsorbed rare-gas atom. A more direct indication comes from Ehrlich and Hudda⁷ who showed that Xe-covered areas of a field-emission tip are brighter than the bare-surface areas of the tip, indicating that Fermi-level conduction electrons see a reduced tunnel barrier or are resonantly scattered at adsorbed Xe. This would of course cause Xe to be visible in the STM.

The experiments were performed using an STM contained in an ultrahigh-vacuum system and cooled to 4 K. The single-crystal metal sample was processed by cycles of heating in a partial pressure of oxygen to remove surface carbon, ion sputtering, and vacuum annealing until it exhibited ostensibly clean Auger spectra and well-ordered low-energy electron-diffraction patterns. After cooling to 4 K, the sample was imaged with the STM and found to be of acceptable quality for the present study. After initial inspection with the STM, the sample, at 4 K, was dosed with typically 1% of a monolayer of Xe. Figure 1 is an STM image of a Xe atom bound to the Ni(110) surface taken under constant-current scan-

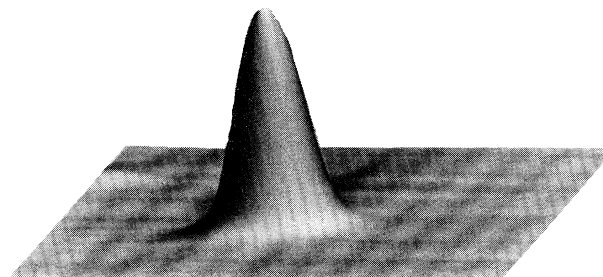


FIG. 1. A $40\text{-\AA} \times 40\text{-\AA}$ constant-current STM image of Xe adsorbed on Ni(110) taken with the tip biased $+0.020$ V relative to the sample and a tunneling current of 1×10^{-9} A. Xe appears as a $1.53 \pm 0.02\text{-\AA}$ -high protrusion. The corrugation of the unreconstructed Ni(110) surface is just visible.

ning conditions. This image was obtained with a tip bias of $+0.020$ V relative to the sample and a tunnel current of 1×10^{-9} A. The Xe atom appears as a nearly cylindrically symmetric 1.53 ± 0.02 -Å-high protrusion from the Ni(110) surface. We have obtained similar images for Xe adsorbed on the Pt(111) surface.⁸

Now Tersoff and Hamann¹ and Lang² have shown that when operated in the constant-current mode the trajectory of the STM tip approximately follows a contour of constant local state density at the Fermi level far outside the surface of a metal. The electronic structure of Xe adsorbed on metal surfaces has been measured by a variety of experimental techniques. Photoemission measurements⁹ demonstrate that the highest filled orbital of adsorbed Xe, the $5p$, lies well below the Fermi level of a metal, typically 6–8 V. Inverse photoemission measurements¹⁰ of Xe adsorbed on Ru(001) show the lowest-lying unfilled state, the $6s$, to lie 4.5 V above the Fermi level. Thus an adsorbed xenon atom makes virtually no contribution to the state density at the Fermi level. Based *only* on this consideration, one would predict that Xe would be virtually invisible in the STM.

In order to clarify why the apparent size of a Xe atom is so substantial we have calculated the electronic structure of an adsorbed Xe atom using the atom-on-jellium model.^{2,3,11,12} In Fig. 2 we display a plot of the Fermi-level conduction-electron density versus distance from the positive background edge of the metal modeled as $r_s = 2$ jellium. The dashed curve is the bare-metal density. The solid curve is a plot of the Fermi-level density through the center of a Xe atom adsorbed at a distance of 5 bohrs from the positive background edge.¹³ This curve exhibits the form and extent to which the conduction-electron density at the Fermi level is redistributed in

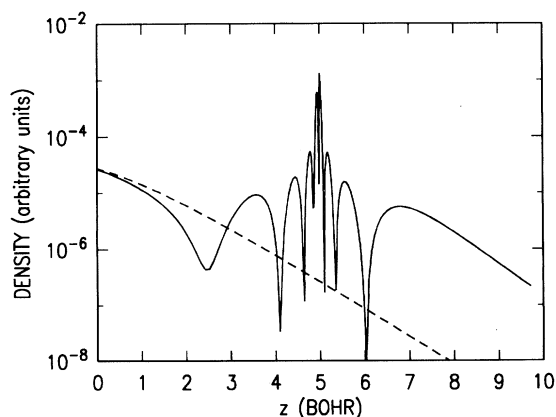


FIG. 2. The Fermi-level conduction-electron density along a normal to the surface through the nucleus of a Xe atom adsorbed at a distance of 5 bohrs from a metal modeled as $r_s = 2$ jellium (solid curve). The bare-metal density (dashed curve) is shown in order to emphasize the form and extent of the conduction-electron density redistribution. The conduction electrons extend further out into the vacuum at the Xe atom.

the vicinity of the adsorbed Xe atom. The most salient aspects of this redistribution are the atomlike oscillations in the density, and, importantly, we see that the conduction electrons at the Fermi level protrude further out into the vacuum at an adsorbed Xe atom than over the bare metal. It is this protrusion which makes Xe visible in the STM.

Lang has shown how the atom-on-jellium model may be used to calculate the apparent height of an adsorbate atom in an STM image.^{2,3} Here we wish to test this theory by making a quantitative comparison of its predictions against our experimental results. To begin, we must estimate the separation of the tip from the sample surface. The STM image of Fig. 1 was recorded with tip-sample resistance of $2 \times 10^7 \Omega$. By measuring the current-versus-height characteristic of the tunnel junction we have determined that this resistance corresponds to the tip being located approximately 7.3 bohrs outward from the onset of the plateau in the resistance of the tunnel junction.^{14,15} Lang has calculated the resistance of such a tunnel junction as a function of the separation of two electrodes modeled as jellium surfaces on one of which a single atom (Na) is adsorbed¹⁴ and has found that a resistance of $2 \times 10^7 \Omega$ corresponds to a tip-surface separation of 8 bohrs from the onset of the resistance plateau. Given this agreement between theory and experiment, we find it reasonable to use Lang's calculated resistance-versus-separation curve as our distance standard. Doing so, we estimate that $2 \times 10^7 \Omega$ corresponds to a distance of 13 bohrs above the positive background edge of the jellium. Let s represent the separa-

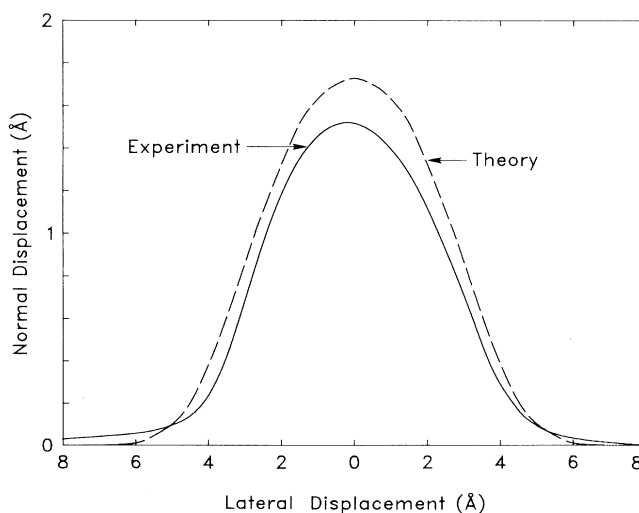


FIG. 3. A comparison of theoretical and experimental normal tip displacement (Å) vs lateral tip displacement (Å) curve for Xe adsorbed on a metal surface. The experimental curve is derived by taking a slice out of the data presented in Fig. 1. The theoretical curve is calculated using the atom-on-jellium model of Lang (Refs. 2 and 3) as described in the text.

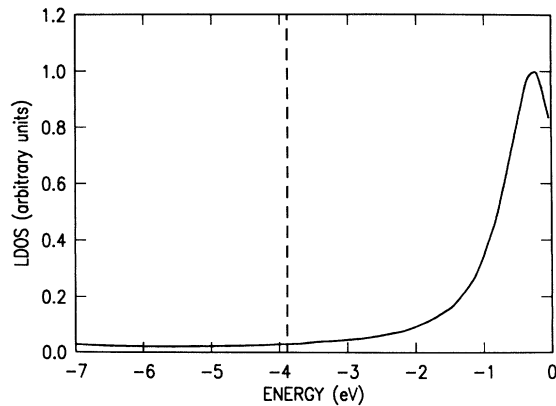


FIG. 4. The calculated additional local density of states (LDOS) [with a barrier penetration term divided out (Ref. 19)] due to an adsorbed Xe atom vs energy measured from the vacuum level. The additional LDOS, that is, the atom-plus-metal minus the bare-metal LDOS, is calculated at a position 11 bohrs directly above a Xe atom adsorbed at a distance of 5 bohrs from the positive background edge of a metal surface modeled as $r_s=2$ jellium. The dashed line indicates the position of the Fermi level. The LDOS at the Fermi level is due to the tail of the almost completely unfilled Xe $6s$ atomic resonance which is seen to peak just below the vacuum level. The residual density of the $6s$ resonance at the Fermi level renders the Xe atom visible to the STM.

tion between the center of the tip atom and the positive background edge of the jellium upon which the Xe is adsorbed. Let Y be the lateral separation between the tip and the Xe atom. Thus a junction resistance of $2 \times 10^7 \Omega$ corresponds to $s(Y=\infty)=13$ bohrs and we will use this as the basis for relating theory to experiment.

In Fig. 3 we display a plot of a contour of constant local state density at the Fermi level corresponding to a value of $s(Y=\infty)=13$ bohrs and compare it with the measured tip trajectory across the center of a Xe atom.¹⁶ We find theory and experiment to be in reasonable agreement. We have found that the shape of both curves in Fig. 3 is not very sensitive to the particular choice of $s(Y=\infty)$.¹⁷ Equivalently, the shape of both curves is not very sensitive (at least in this regime) to the tunnel-junction resistance.

Finally, we consider the physical origin of the Fermi-level state density which gives rise to the observed size of a Xe atom in an STM image. To do so, we plot in Fig. 4 the energy dependence of the additional local state density, that is, the local state density of the Xe-metal system minus the bare-metal local state density, at a position 11 bohrs directly above the adsorbed Xe atom.¹⁸ A barrier penetration factor has been divided out.¹⁹ We see that the local state density at the Fermi level is due to the broadened $6s$ resonance,^{4,20} the peak of which lies less than 0.5 V below the vacuum level. An additional indication that the state density at the Fermi level is due to the broadened $6s$ is that the location of the maxima and

minima in the density distribution exhibited in Fig. 2 correspond to those of the $6s$ orbital of Cs.²¹

Despite the fact that the $6s$ resonance is virtually unfilled, we see that it dominates the local state density on the vacuum side of the adsorbed Xe atom. This happens for two reasons. First, Xe binds at relatively large distances from metal surfaces. Second, the size of the Xe $6s$ resonance is comparatively large. These two circumstances combine to make it such that even a very small filling of the resonance can result in the $6s$ local state density being substantially greater than the bare-metal local state density on the vacuum side of the atom.²²

We have presented the first quantitative comparison of STM images of single-atom adsorbates with the theory of Lang.^{2,3} The excellent agreement we find not only confirms our belief that the theory contains all the essential elements for understanding STM images of single-atom-on-metal systems but also confirms the applicability of the Tersoff-Hamann approximation¹ in this regime. In addition, we learn that even though an atomic resonance of an adsorbate atom lies far from the Fermi level, it may nevertheless make the dominant contribution to an STM image if the size of the orbital associated with that resonance is such that it extends considerably further out into the vacuum than the bare-surface wave functions.

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²N. D. Lang, Phys. Rev. Lett. **56**, 1164 (1986).

³N. D. Lang, Phys. Rev. Lett. **58**, 45 (1987); Comments Condens. Matter Phys. **14**, 253 (1989).

⁴We note that the asymmetric environment of an adsorbate atom will cause the atomic resonances of that atom to be states of mixed symmetry. For simplicity, we choose to denote a resonance by the free-atom orbital from which it was predominantly derived. (The resonance denoted $6s$ here also has $6p$ and $5d$ components.)

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¹³The equilibrium distance of Xe above $r_s = 2$ jellium was estimated to be approximately 5 bohrs in Ref. 11.

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¹⁵J. K. Gimzewski and R. Möller, Phys. Rev. B **36**, 1284 (1987).

¹⁶It was shown in Ref. 2 that the Fermi-level state-density contours are a reasonable approximation to the tip trajectory.

¹⁷The theoretical apparent height of the xenon atom increases by about 0.1 bohr for each bohr decrease in $s(Y = \infty)$. The experimental apparent height of the xenon atom increases about 0.2 bohr for each bohr decrease in $s(Y = \infty)$. There is no significant dependence of the apparent height of the xenon atom on the magnitude or polarity of the applied voltage within the range ± 0.1 V; this is because the local state density is only slowly changing at the Fermi level.

¹⁸This corresponds to the height of the tip at the position corresponding to zero lateral separation in Fig. 3.

¹⁹The energy dependence of the local density of states (LDOS) at large distances is dominated by the energy dependence of the barrier penetration factor, which we can approximate at $\exp(-2z\sqrt{-2E})$, using atomic units, where z is an appropriate distance and E is energy relative to the vacuum. Since we are interested in the structure of the LDOS beyond

that contained in this exponential factor, we have divided out this factor in the data presented in Fig. 4. (Unless we do so, the curve would simply rise rapidly to the right, swamping the peak structure seen here.) Now of course the shape of the curve at energies well below the vacuum level depends on the choice of origin of z ; we have chosen it on physical grounds to be at the outer edge of the empty $6s$ shell, whose radius we approximate by the covalent radius of Cs (2.4 Å).

²⁰Adsorbed He is quite different from the heavier rare gases in that its empty density of states just below the vacuum level shows no resonance. The additional LDOS over nearly the entire energy range between the Fermi level and the vacuum level is in fact negative; i.e., He has the effect of decreasing the amplitude of the metal states in the vacuum region. Thus He would be expected to appear as a dip in an STM image rather than a bump. (See discussion of this in Ref. 2.)

²¹F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, NJ, 1963).

²²To check whether any local change in the tunneling barrier due to the dipole moment of the single adsorbed Xe could make a significant contribution to the tip displacement, we recalculated the LDOS in the presence of a Xe atom with no dipole moment (we just used the free-atom density). Only a very small decrease in the LDOS at the Fermi level occurred, corresponding to a change in tip displacement of less than 0.1 bohr.

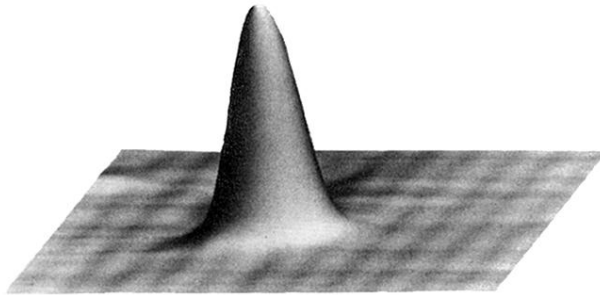


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