Interaction of Xenon at Surface Steps

Peter Zeppenfeld, Sebastian Horch, and George Comsa
Institut für Grenzflächenforschung und Vakuumphysik, Kernforschungsanlage-Forschungszentrum Jülich,
D-52425 Jülich, Germany
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The adsorption of Xe on Pt(111) has been investigated using scanning tunneling microscopy. At low coverage Xe preferentially adsorbs on the *upper edge* of the preexisting Pt steps resulting in the formation of one-dimensional chains of Xe atoms. With increasing coverage the adsorption proceeds with the growth of compact 2D Xe islands nucleated on the Pt terraces and at the *lower* Pt step edges, but not adjacent to the Xe chains on the *upper* terraces. This is indicative of a repulsive interaction between the Xe chains and Xe atoms on the upper Pt terrace.

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The rare gases have a long tradition in serving as model systems in condensed matter physics. This model character is based on their spherical symmetry and the simple electronic structure. At surfaces the rare gases have been used as testing grounds in such different fields as the kinetics of adsorption and desorption, thin film growth and wetting, two-dimensional (2D) structures, and 2D phase transitions [1,2]. Usually, the same central-symmetric pair potentials established for the gas phase are also used to describe the interaction of the rare gases at surfaces. To a first approximation the mutual interaction between the adsorbed rare gas atoms as well as the interaction of a rare gas atom with the surface atoms could then be treated as the sum over the corresponding pairwise contributions.

Early, however, it became apparent that this mere sum of pairwise interactions cannot reproduce the experimental values of the binding energies but that many body terms, substrate mediated interactions, and surface dipole interactions can make a significant contribution [3]. Nevertheless, it was believed that these contributions would not alter the overall qualitative picture. In particular, it was implicitly assumed [1] that the rare gases were preferentially bound at high coordination sites on the surface and that the net interaction between adsorbed rare gas atoms would be attractive.

Indeed, the formation of compact 2D islands and, hence, attractive interactions are observed for the rare gases adsorbed on graphite and numerous metal surfaces. On the other hand, it has been shown that on the low-indexed Pd surfaces Xe forms a stable dilute phase even at very low temperatures, suggesting a *repulsive* interaction between Xe atoms adsorbed on Pd [4,5]. Another intriguing issue was raised recently, namely, the possibility for a single Xe atom to be preferentially bound at low coordination sites on metal surfaces [5–8]. In an *ab initio* cluster calculation [6] Müller found that the on-top site should be the energetically preferred binding site for a Xe atom on Pt(111). Further evidence for a Xe on-top position was obtained by Barker and Rettner [7] from fitting an empirical Xe-Pt potential to the large body of experimental data available for the Xe/Pt(111) system.

On the other hand, direct *experimental* evidence for an on-top adsorption site for Xe on metal surfaces has remained rather scarce. The available information is based mainly on the analysis of spin polarized low energy electron diffraction (SPLEED) intensities [5] and He diffraction patterns [8]. Besides, for Xe adsorbed on the Ni(110) surface scanning tunneling microscopy (STM) images obtained with low temperature STM [9] are suggestive of a low coordination site for a single adsorbed Xe atom.

Here we report an STM investigation of the adsorption of Xe on the Pt(111) surface which provides direct experimental evidence for the preferential binding of a Xe atom on the low-coordinated *upper* step edge and a resulting local *repulsive* Xe-Xe interaction. The latter is remarkable in view of the well established attractive interaction between Xe atoms on Pt(111) terraces.

The experiments were carried out using a variable-temperature STM [10] contained in an ultrahigh vacuum chamber (base pressure $< 10^{-10}$ mbar). We use a modified version of the "beetle" STM in which the sample is fixed and the microscope is posed on the sample holder [11]. The sample itself is mounted on a manipulator and can be cooled to 10 K by means of a He flow-through cryostat to which it is connected by a copper braid. During sample preparation (i.e., with the STM temporarily removed) the sample can be heated up to 1200 K by electron bombardment from the back side of the crystal. The STM can be operated at any sample temperature between 10 and 400 K either by tuning the He flow or by computer-controlled regulation of the sample heating. The surface temperature is measured with a Ni-CrNi thermocouple spot welded to the crystal.

The high quality Pt(111) crystal was cleaned by repeated cycles of 1 keV Ar-ion sputtering and heating in oxygen. The surface order and cleanliness was checked *in situ* by LEED and Auger spectroscopy. Once the impurity concentration had dropped below the sensitivity level of the cylindrical mirror analyzer Auger spectrometer the STM was used to further control the preparation procedure. Finally, large clean terraces with an average

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separation ≥ 1000 Å separated by smooth atomic steps were rountinely obtained. Xe was adsorbed by exposing the cold surface to a partial pressure of the rare gas using a leak valve. The valve was closed and the Xe pressure pumped off once the desired coverage was reached.

Figure 1 shows an STM micrograph obtained after adsorption of about 0.06 monolayer (ML) of Xe on Pt(111) and subsequent annealing at 29 K. A few Xe islands have nucleated on the Pt terraces. They can be recognized by the more ragged rim as compared to the straight step edges separating neighboring Pt(111) terraces. More importantly, the Pt step edges are decorated by a thin line of Xe atoms forming a type of atomic "pearl chain." Note that the population of these edge sites is very high considering the small overall Xe coverage. A similar behavior was already observed in a previous low temperature (4 K) STM study of the Xe/Pt(111) system by Weiss and Eigler [12]. There, the principal question was how the Xe atoms could reach the Pt step edges at all, since the thermal mobility of Xe on Pt(111) at 4 K is expected to be negligibly small. A convincing explanation was presented in [12] in terms of the *transient mobility* gained by the Xe atoms as a consequence of the conversion of the binding energy released upon adsorption into lateral kinetic energy [13]. In the present study, we have observed the preferential decoration of the Pt step edges with Xe for all adsorption temperatures in the range between 10 and 70 K, i.e., even for thermally well equilibrated Xe adlayers. This strongly suggests that the Pt step edges provide, indeed, energetically preferred binding sites for the Xe atoms (rather than just being a location at which the hyperthermal kinetic energy is efficiently dissipated).

In Fig. 2 we present a series of four STM micrographs which shows how the initial decoration of the upper step edges proceeds as a function of the xenon coverage. To this end we have first prepared a surface with an enhanced density of atomic steps by sputtering the Pt(111) surface at 735 K with 1 keV Ar ions, thereby removing a fraction of a Pt monolayer. Under the given experimental conditions vacancy islands (holes a single layer deep and a few hundred Å in diameter) are created [14]. In Fig. 2 one of these vacancy islands is imaged after successive adsorption of Xe at 10 K. In this experiment Xe was adsorbed with the STM still positioned above the sample to ensure that the STM images were recorded at the same place on the surface (only the tip was temporarily retracted by a few hundred Å). The Xe flux striking the surface area to be imaged is now reduced due to the partial shadowing of the sample by the STM. Consequently, the local coverage cannot be calculated from the Xe exposure directly and has been roughly estimated from the STM images themselves. After adsorption of about 0.01 ML of Xe the image in Fig. 2(a) was obtained. Even for such low coverage most of the Pt step edges forming the rim of the vacancy island are already decorated with Xe

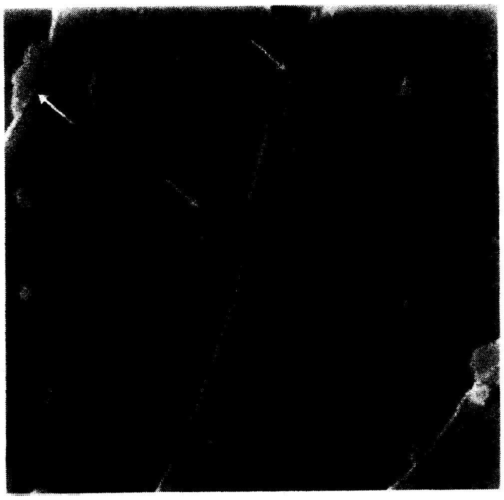

FIG. 1. STM micrograph (1500 Å×1500 Å) of a Pt(111) surface covered with about 0.06 ML of Xe adsorbed at 17 K and annealed at 29 K. The image was recorded at 17 K (tip bias $V = -0.2$ V, tunneling current $I = 1$ nA). The STM signal is high-pass filtered such that the surface appears to be illuminated from the left. Several Xe islands have nucleated on the Pt terraces and some have grown from the Pt step edge onto the lower Pt terrace (arrows). The *upper* Pt step edges are decorated with a single atomic chain of Xe atoms.

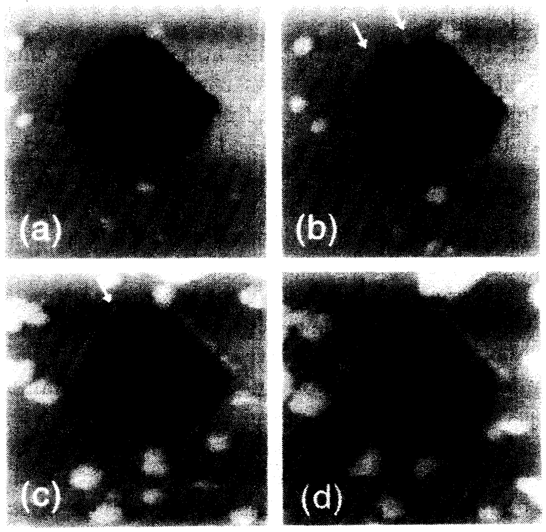

FIG. 2. Series of STM micrographs (360 Å×360 Å) showing the evolution of the surface morphology of a Pt(111) surface during Xe adsorption. The four images are recorded on the same area of the surface after adsorption of about 0.01 ML (a), 0.02 ML (b), 0.15 ML (c), and 0.2 ML (d) of Xe at 10 K. Tunneling parameters: tip bias $V = -0.4$ V, tunneling current $I = 1$ nA; all images were recorded at 10 K. Note the preferential adsorption of Xe atoms at the upper step edge of the Pt vacancy island and the incorporation of additional atoms (arrows) with increasing Xe coverage.

atoms. Figure 2(b) was recorded after increasing the Xe coverage to about 0.02 ML. It shows that at a few places individual Xe atoms have been added to the step edge (bright spots indicated by the arrows in Fig. 2). Further increase of the Xe coverage [Fig. 2(c)] results in an additional, although not complete, filling of the Xe atomic chain around the vacancy island. (In fact, even in the closer-packed regions of the chain the average separation between Xe atoms is still above 10 Å.) At the same time the Xe islands that have nucleated on the Pt terraces grow larger in size and, eventually, new Xe areas start to grow out from the lower step edge onto the lower Pt terrace (i.e., towards the center of the vacancy island), but not from the step edge onto the upper terrace [Fig. 2(d)]. The latter aspect is most evident from Fig. 3 (recorded at higher Xe coverage and after annealing). Here the Pt vacancy islands are almost completely filled with Xe while on the upper Pt(111) terraces only Xe islands nucleated far away from the rim of the Pt vacancy islands are observed.

At first sight, this result does not seem to be surprising at all, since it is a common observation that the nucleation and growth of an adlayer starts at the lower side of a surface step where the atomic coordination is highest. However, we will now demonstrate that in the present case the decoration of the Pt step edge with Xe occurs at the *upper* side of the step rather than on the *lower* side. Furthermore, the decoration is limited to a single chain of Xe atoms which, therefore, does not serve as a "nucleation line" for the growth of 2D Xe islands on the upper Pt terrace.

As indicated by the arrows in Fig. 1 and apparent from Figs. 2 and 3 Xe areas eventually grow out from the Pt step edge onto the lower Pt terrace. Figure 3 shows two STM images obtained after adsorption of about 0.45 ML Xe at 13 K and successive annealing at 32 and 40 K, respectively. The rim of the vacancy islands created on the Pt surface prior to the Xe adsorption as well as two step edges on the Pt surface running across the images in Fig. 3 are clearly evidenced by the Xe atomic chains. After annealing the surface, 2D Xe areas have formed at the lower side of the Pt vacancies' rims, partially filling the vacancy islands and completely covering the lower Pt step edges. These Xe areas are quite smooth. This had to be expected on the basis of a previous He-scattering study of the Xe/Pt(111) system [2], which showed that under the above experimental conditions the Xe adlayer exhibits a well ordered, close-packed structure. Within experimental accuracy the Xe covered areas located on the lower terrace (i.e., inside the Pt vacancy island) are imaged at the same height as the adjacent, noncovered, upper Pt terrace. Only the Xe chain at the Pt step edge appears to be 1–2 Å higher. The fact that the Xe atoms located at the Pt step edge appear higher than the adjacent Xe covered area, however, does not necessarily imply that the Xe atoms are adsorbed at the upper edge of the step. One might still ascribe the increased height in the STM image to an electronic effect due to the presence of the Pt step and assume that the Xe atoms are adsorbed at the more "cosy" location in the lower part of the Pt step [12]. However, this assumption is at variance with two observations evident from the STM image in Fig. 3: (i) Along all borders between the Xe areas and the adjacent upper Pt terraces the Xe chains are more or less discontinuous; i.e., Xe atoms are missing from the chains. In fact, at those places where no Xe chain is present the transition between the Xe island and the upper Pt terrace across the Pt step edge is virtually invisible in the STM image. Since the Xe areas nucleated at the lower edges of a Pt step are densely packed it is hard to imagine that some of the Xe atoms in this smooth Xe area should be missing right at the lower step edge. Therefore, the Xe atomic chain appearing higher in the STM images must be located at the *upper* edge of the Pt step (where, of course, the Xe atoms do not have to form a perfectly continuous chain). (ii) The Xe atoms in the chain are quite mobile and can rearrange themselves upon annealing even if large 2D Xe areas have already formed on the lower terrace. This is obvious from Fig. 3 where many of the Xe chains along the rim of the Pt vacancy islands have changed their appearance after the sample was annealed at 40 K. In particular, the step edge where the Xe chain was previously missing [arrow in Fig. 3(a)] is partially decorated by Xe atoms after annealing [arrow in Fig. 3(b)]. Since this decoration of the Pt step edge occurs while the *lower* step edge is already covered by a dense 2D Xe area, only the *upper* edge can provide empty adsorption sites. Therefore, the Xe atomic chain must, indeed, be located at the upper edge of the Pt step.

Note that this Xe atomic chain remains atomically thin

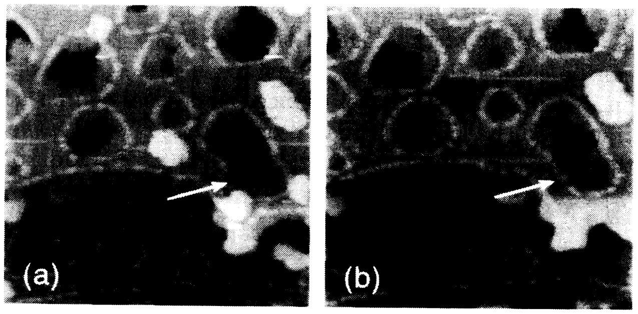

FIG. 3. Two STM images (920 Å×920 Å) of a Pt(111) surface covered with about 0.45 ML of Xe adsorbed at 13 K and successfully annealed at 32 K (a) and 40 K (b). The images were recorded at 13 K (tip bias $V = -0.4$ V, tunneling current $I = 0.8$ nA). The Pt vacancy islands are partially filled with Xe; the rim of the vacancy islands is decorated by a single, discontinuous atomic chain of Xe atoms located at the *upper* edge of the Pt step. The arrows indicate how the annealing can change the structure of the Xe chain (see text).

even for large Xe coverage and elevated annealing temperatures (see Figs. 1–3). This means that the attachment of additional Xe atoms next to the Xe chain and, hence, the growth of 2D Xe areas from the Xe chain onto the *upper* Pt terrace is energetically inhibited. This suggests an effective repulsive interaction between the Xe atoms in the atomic chain and Xe atoms approaching it from the upper terrace. Since the Xe-Xe interaction is clearly attractive in the gas phase as well as on the flat Pt(111) terraces [2], this local repulsive force must arise from the particular bonding situation of a Xe atom at the upper step edge. An intuitive explanation would be to expect the stronger binding of the Xe atom at the upper step edge to result in an enhanced Xe-metal surface dipole. As a consequence, neighboring Xe atoms would experience a stronger repulsive dipole-dipole force which could eventually outweigh the direct Xe-Xe attraction. Such a relationship between the strength of the Xe binding energy, the size of the surface dipole moment, and the resulting Xe mutual repulsion was also conjectured from a comparison of the adsorption properties of Xe on various flat metal substrates [15].

Finally, we want to emphasize that the present results fit well into the more refined theoretical picture of the Xe bonding to metal surfaces, which has evolved during the last decade: Following the self-consistent calculations by Lang [16] and Müller [6], the binding of the rare gases to metal surfaces bears a strong covalent character, which is reflected in a local charge transfer between the rare gas atom and the metal surface as well as a lateral redistribution of the charge within the surface. While the calculations in Ref. [16] were performed for a flat jellium surface, a (111)-oriented cluster containing more than twenty Pt atoms was used in Ref. [6] to specifically model the Pt(111) surface. The calculation of the binding energy for a Xe atom on different sites on the Pt cluster reveals that Xe preferentially binds at the on-top position [6]. Moreover, the strongest binding site is found right at the edge of the Pt cluster [17], which can be compared to some extent to an upper step edge on a real Pt(111) surface. Hence, Xe appears to be attracted to the low-coordinated or "exposed" sites rather than the high-coordinated or "cosy" sites. In addition to the binding of a single Xe atom, Müller also discusses the effect of a second Xe atom binding next to the first one. He finds [6] "that the Xe-Xe interaction is very sensitive to the charging of the adatoms. This means that on surfaces more reactive than Pt (for instance, Pd) or on locations of larger adsorption energy (as in surface steps) the Xe-Xe interaction may indeed become repulsive."

We are delighted to acknowledge helpful conversations with Jorge Müller.

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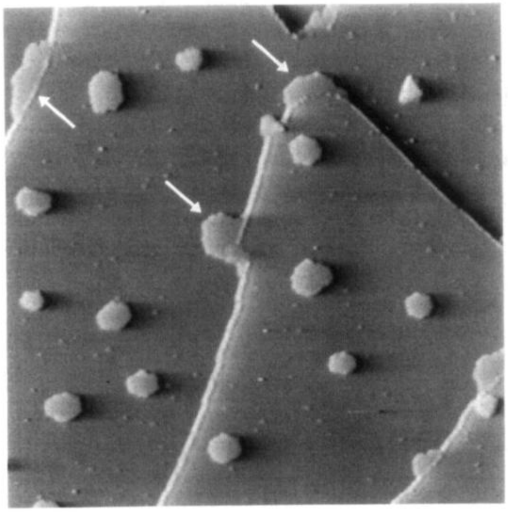

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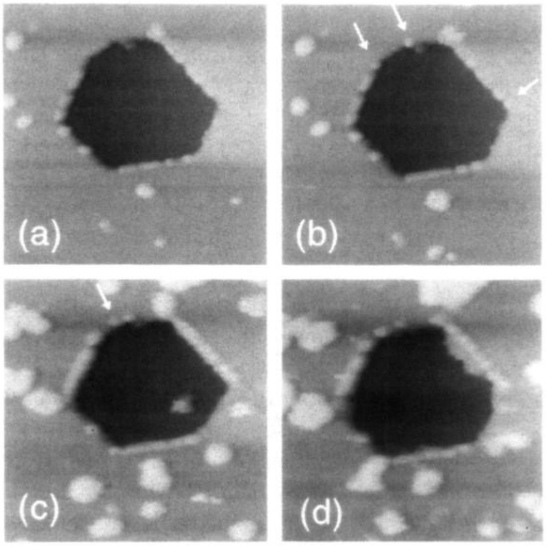

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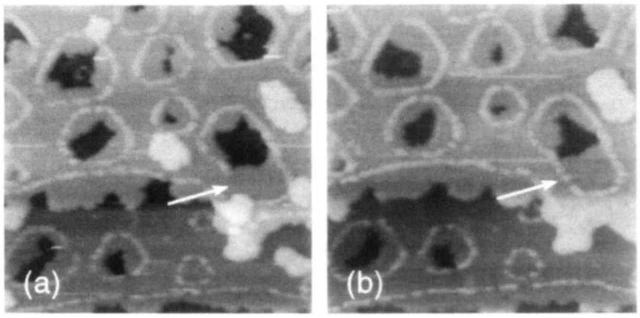

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