

Remarkably long-ranged repulsive interaction between adsorbed CO molecules on Pt modified Ge(001)

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We have studied the adsorption of CO molecules on a Pt modified Ge(001) surface at 77 K. The CO molecules preferentially adsorb on the self-organized Pt chains rather than on the terraces. We have identified two different adsorption sites at 77 K: one either on the short-bridge site or on top of one of the atoms of a buckled Pt dimer, and the other one on the long-bridge site in between two Pt dimers. The CO molecules are mobile at room temperature but immobile at 77 K. A statistical analysis of the nearest-neighbor spacing of the CO molecules reveals that adsorbed CO molecules interact repulsively along the Pt-dimer chains. This repulsive interaction, composed of electrostatic terms and a strain-mediated term, gradually fades away over, for simple molecules, a remarkably long distance of 3–4 nm.

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I. INTRODUCTION

The adsorption of molecules on surfaces is a key step in many important industrial processes, such as catalysis and metal organic chemical vapor deposition (MOCVD), and, therefore, many studies have been devoted to this topic. The adsorption of carbon monoxide (CO) on platinum (Pt) is probably the most thoroughly investigated model system.^{1–9} Already in the early 1900s Langmuir¹ studied the mechanism of a catalytic reaction involving CO and Pt. During the last decades, both experimental and theoretical studies have been performed in order to obtain a better understanding of the behavior of adsorbed CO on Pt.^{2–13} The majority of these studies, however, have been devoted to single-crystal surfaces. The adsorption of CO on Pt(111) has been particularly well studied (Ref. 9, and references therein). At low coverage, CO prefers to adsorb on atop sites but at higher coverages the bridge site is occupied as well. Despite an ongoing dispute on the exact nature of the mutual interaction between coadsorbed CO molecules on Pt(111), it has been well established that CO molecules experience mutual repulsion. The range of this repulsive interaction is rather short. The occupation of nearest-neighbor sites is excluded but next-nearest ones are allowed, yielding a repulsive range of about 0.5 nm. Some larger molecules on surfaces, as, for instance, tetrathiafulvalene molecules on Au(111), exhibit repulsive interactions which have a much longer range.^{14,15}

The adsorption of CO on transition metals is often described in terms of the Blyholder model.¹⁶ To describe the adsorption of CO on metal surfaces, Blyholder¹⁶ extended the Dewar-Chatt-Duncanson model of the chemical bonding between alkenes and metals.^{17,18} In this donation/backdonation model, electrons are donated from the highest occupied molecular orbital (HOMO) of CO, 5σ , to the d_z^2 orbital of the metal. Subsequently, electrons are backdonated from the metal $d\pi$ orbital to the lowest unoccupied molecular orbital (LUMO) of CO, i.e., $2\pi^*$. Within this Blyholder model the repulsive interaction between adsorbed CO molecules can be understood in a straightforward manner: the adsorbed molecules form a dipole with an estimated dipole

moment of 0.9 D for Pt.¹² For a CO molecule that adsorbs at an on-top site, this dipole moment is aligned in a direction perpendicular to the surface. Due to this parallel alignment, neighboring CO molecules undergo mutual repulsion. In addition, the adsorption induces local charge rearrangements that lead to electrostatic interaction as well.¹⁹

As mentioned before most studies were performed on single-crystal Pt surfaces. Studies on compound systems involving Pt have, however, attracted less attention. In this paper we present a study of the adsorption of CO on a Pt-material based surface. For this purpose, we have grown arrays of Pt chains on a Ge(001) surface. These linear Pt chains, with a cross section of just one atom, consist of Pt dimers, and are virtually defect and kink free and can reach lengths up to a micron. The chain-to-chain separation is 1.6 nm.^{20–22} The Pt/Ge(001) system might be an attractive candidate for molecular electronic applications. We have attempted to decorate these Pt chains with organic molecules. CO is an attractive and simple molecule candidate since it prefers to stick to Pt and has no tendency to react with Ge. Our study indeed reveals that CO binds preferentially, if not exclusively, to the Pt chains. The CO molecules are mobile at room temperature, and perform a one-dimensional random walk along the Pt chains. An analysis of these diffusion data indicates that CO molecules repel each other. The range of this repulsion is spectacular: CO molecules show a mutual repulsion at distances as large as 3–4 nm. In comparison, CO molecules adsorbed on Pt(111) exhibit a repulsive interaction that vanishes within a distance of less than 0.5 nm.

In order to investigate this repulsive interaction in more detail, we have investigated the adsorption of CO well below room temperature. At low temperatures the CO molecules adsorb on the chains as well but in contrast to room temperature they are immobile. An additional complexity is that at low temperatures we observed two different adsorption sites on the chains. None of these two low-temperature adsorption sites corresponds to the one occupied at room temperature. This remarkable observation is attributed to the different electronic and structural properties of the Pt chains at room temperature and 77 K, respectively.²⁴

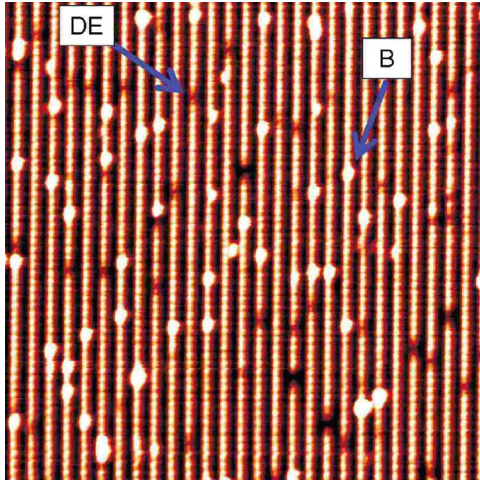


FIG. 1. (Color online) Empty state STM image ($45.5 \times 45.5 \text{ nm}^2$; $+1.8 \text{ V}$; 0.5 nA) of a Pt/Ge(001) surface covered with CO-decorated Pt chains of platinum, recorded at 77 K . The exposure to CO was done at room temperature. The CO molecules adsorb to the Pt chains in two different configurations; at positive bias one configuration shows up as a depression (black holes; DE) while the second configuration shows up as a protrusion (white spots; B).

II. EXPERIMENTAL METHOD

We have studied the adsorption of CO on the Pt/Ge(001) system with an Omicron low-temperature scanning tunneling microscope (LT-STM). The $5.0 \times 10.0 \text{ mm}^2$ Ge(001) substrates were cut from nominally flat single-side polished n -type wafers. The samples were first slowly degassed after having been placed into the ultrahigh vacuum (UHV) setup. Subsequently, the samples were sputtered with 800 eV argon ions and annealed for 2 min to 1100 K using a dc current. This cleaning procedure was repeated several times until atomically clean and well ordered Ge(001) surfaces were obtained. Imaging with STM at both room temperature and at 77 K revealed that three different well ordered domain patterns were formed: (2×1) , $p(2 \times 2)$, and $c(4 \times 2)$.²³

After cleaning, a submonolayer amount of Pt was evaporated onto the room-temperature Ge(001) surface from a Pt wire wrapped around a tungsten filament. After evaporation the Pt/Ge(001) substrate was annealed at 1100 K for 2 min and subsequently cooled down to room temperature. Following this procedure we found large regions that contain arrays of Pt chains.

In the next step the sample was exposed to 2750 Langmuir CO at 293 K . The CO was introduced at room temperature into the preparation chamber of the UHV system via a leak valve. After exposure to CO, the samples were first imaged at room temperature and subsequently cooled down to 77 K . After thermal equilibration, the samples were imaged again.

III. RESULTS

Figure 1 shows a Pt/Ge(001) surface imaged at 77 K with a sample bias of $+1.80 \text{ V}$ (empty state image) after exposure to 2750 Langmuir CO. The imaged area is fully covered with

monatomic Pt chains that are spaced apart by 1.6 nm . Immediately apparent are two types of spots on the Pt chains. Both types have not been observed before CO exposure. First, there are quite a number of dark features, appearing as depressions in the chain. Second, bright protruding spots on the chains are observed. For convenience we will now coin these dark and bright features DE and B, respectively. The background was continuously monitored during the adsorption process and no gases other than CO were detected. As such, both features must be related to the adsorption of CO molecules on the Pt chains. First of all it appears that the abundance of DE and B species is about equal. In Fig. 1 there is only one bright feature that is not located on top of the Pt chains but in between the Pt chains (in the center of the image). The latter might either be a regular CO molecule, an adsorbed foreign molecule, or a defect. The B-type adsorption site is not found at room temperature.²⁰ Since the abundance of the two species is about equal, it is likely that both adsorption sites, i.e., DE and B, have comparable binding energies. Since the Pt chains undergo a phase transition from a $2 \times$ periodicity at room temperature to a $4 \times$ periodicity at low temperatures,²⁴ it is tempting to relate the feature B to the adsorption on the $4 \times$ Pt chains. The $4 \times$ chains are comprised of buckled Pt dimers, whereas the Pt dimers of $2 \times$ chains are unbuckled.

The B and DE features were studied in more detail by imaging them at both positive and negative sample biases. In Fig. 2 we show a DE feature measured at (a) -1.80 and (b) $+1.80 \text{ V}$. The most prominent difference between the negative and positive biases is given by the fact that the DE feature shows up as a depression in an empty state image and as a protrusion in a filled state one. Less prominent is a slight curvature along the chain that is observed at negative biases. These observations are in agreement with the room-temperature data published by Oncel *et al.*²⁰ Oncel *et al.*²⁰ attributed these observations to a CO molecule adsorbed at a short-bridge site in the Pt-dimer chain. The latter is also in good agreement with a recent first-principles density-functional study of the interaction between an isolated monatomic Pt chain and a CO molecule by Sclauzero *et al.*²⁵ These authors²⁵ compared the energies of different adsorption sites (bridge, substitutional, tilted bridge, and on top) and found that for an unstrained wire the bridge site is energetically the most favorable one. It should be pointed out that the calculations in Ref. 25 are for an isolated infinite Pt wire, whereas our experiments are performed on Pt wires that are grown on a Ge(001) substrate. Therefore, one should be somewhat cautious in comparing these two data sets.

Figure 3 presents feature B scanned at (a) -1.80 and (b) $+1.80 \text{ V}$. Contrary to DE, the B feature shows up as a protrusion at both negative and positive sample biases. The B-type feature is not present in the room-temperature data of Oncel *et al.*²⁰ As will be shown later, also the DE feature is not related to the short-bridge adsorption site that is observed at room temperature.

In Fig. 4 we compare the height profiles of several line scans taken along the Pt chain. We show the profiles of two chains with an adsorbed CO: one along a DE feature (dotted line) and the other along the B feature (dashed line). As a reference we plotted the height profile of a bare Pt chain

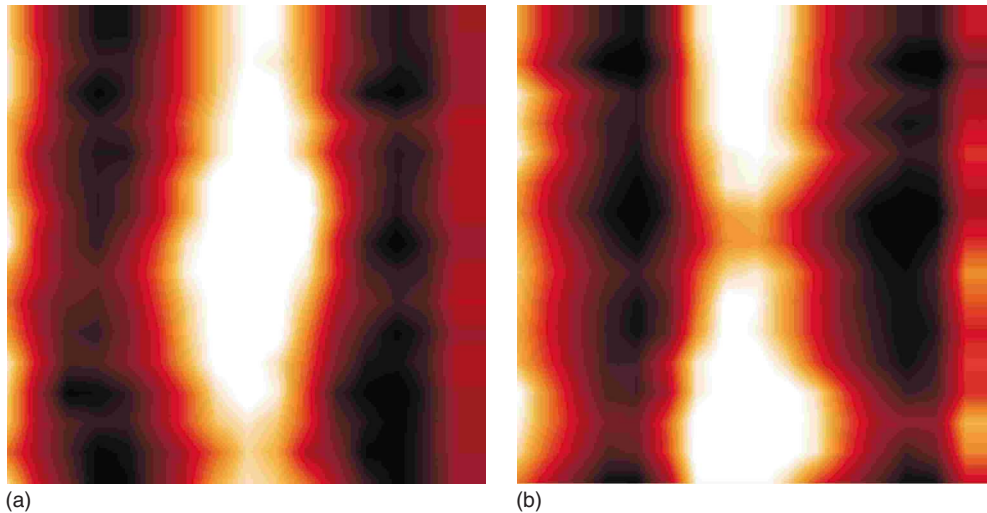


FIG. 2. (Color online) STM images ($2.7 \times 2.7 \text{ nm}^2$) of a CO molecule (feature DE) adsorbed on a Pt chain, imaged at 77 K, 0.50 nA, and (a) -1.80 and (b) $+1.80$ V. This molecule shows up as a small protrusion at (a) -1.80 V and as a depression at (b) $+1.80$ V.

(solid line). Note that a pair of buckled Pt dimers forms the elementary building block of a $4 \times$ Pt chain.

It is clear that the *minimum* in the height profile of DE is exactly positioned at a minimum of the profile of the bare Pt chain, i.e., in between two adjacent Pt dimers. This position is referred to as long bridge. For profile B the situation is less straightforward. First of all, we note that the feature exhibits two rather broad lobes. We emphasize that the mirrored situation, i.e., with the maximum intensity on the left-hand side occurs with about the same probability. The *maximum* is positioned above a maximum of the profile of the bare chain, i.e., on top of a Pt dimer. The two lobes and the asymmetric appearance of this feature indicate that the CO molecule is probably slightly tilted or adsorbed at one of the two atoms of the Pt dimer. Since most of the Pt dimers are buckled at 77 K, no clear distinction between an on-top adsorption site and a short-bridge adsorption site can be made.

Summarizing, at room-temperature CO adsorbs at a short-bridge site, showing up as a depression at positive bias and

as a protrusion at negative bias. At 77 K, this adsorption site is no longer present while two other adsorption sites appear. First, a long-bridge site shows up as a protrusion at negative bias and as a depression at positive bias. Second, we found a short-bridge (or on-top) site, which emerges as a protrusion at both negative and positive biases.

At room temperature the CO molecules perform a random walk on the Pt chains.²⁰ However, at 77 K the CO molecules lack mobility. More than 100 CO molecules were monitored during approximately 90 min. We found no indication for any thermally activated motion. Using several low-temperature images, as the image shown in Fig. 1, the distribution of the nearest-neighbor separation between adsorbed CO molecules on the same Pt chain was determined. For 390 CO molecules the distance to their nearest-neighbor CO molecule on the same Pt chain was measured.

In Fig. 5 we have plotted the experimentally determined probability distribution. In addition, we have plotted the probability distribution that one would expect in case neigh-

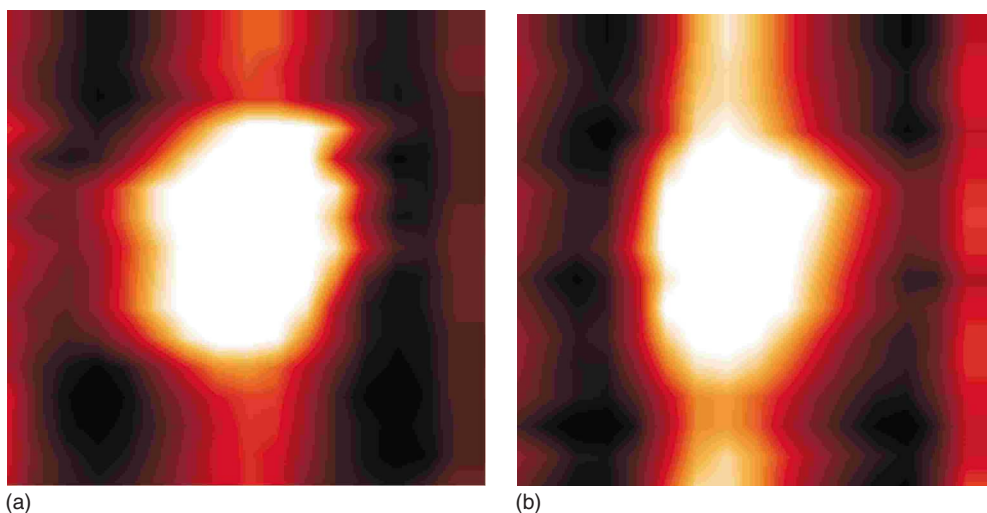


FIG. 3. (Color online) STM images ($2.7 \times 2.7 \text{ nm}^2$) of a CO molecule (feature B) adsorbed on a Pt chain, imaged at 77 K, 0.50 nA, and (a) -1.80 and (b) $+1.80$ V. This molecule shows up as a protrusion at both -1.80 and $+1.80$ V.

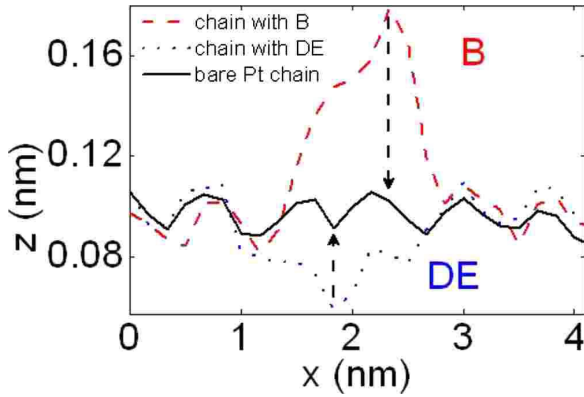


FIG. 4. (Color online) Line profiles taken along three different Pt chains at 77 K; chain with an adsorbed DE-CO molecule (dotted curve), chain with an adsorbed B-CO molecule (dashed curve), and chain without CO (solid curve). Sample voltage is 1.8 V while sample current is 0.50 nA.

boring adsorbed CO molecules do not interact. The probability of finding a CO molecule at any site on the Pt chain is given by p (p is the probability of finding a Pt-chain site covered and equals 0.078 in our experiment). The probability to find two neighboring CO-occupied adsorption sites is thus simply given by p^2 . The probability to find a separation by two lattice sites is then given by $(1-p)p^2$. Finally, the probability to find a separation of M lattice sites is $(1-p)^{M-1}p^2$. In order to obtain a normalized distribution function, the above numbers have to be divided by p .

It is immediately clear from the data that the CO molecules adsorbed on the same Pt chain repel each other on a length scale up to about 3–4 nm. Since (repulsive) interaction between adsorbed CO molecules on neighboring chains is virtually absent, the repulsive interaction along the chain cannot be solely electrostatic in origin. We have fitted the repulsive interaction by taking into account two terms: a dipole-dipole term which decays as L^{-3} and a strain-mediated term which falls off logarithmically along the chain

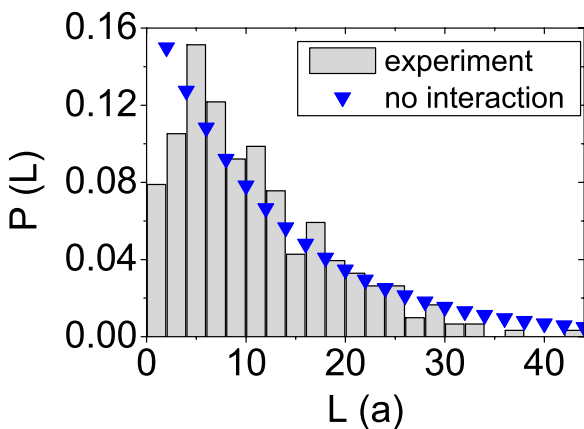


FIG. 5. (Color online) Normalized probability distribution for nearest-neighbor spacing of CO molecules on the same Pt chain; shown are both experimental data (bars) and a “no interaction” model (triangles). In this plot the distance is normalized to the spacing between adjacent Pt dimers within a Pt chain (=0.8 nm).

direction. Despite the fact that we have only a limited data set (separations in the range from 0.8 to 4 nm), the data can be fitted properly with a combination of an electrostatic dipole-dipole interaction and a strain-mediated interaction. Since we have two different CO adsorption sites on the Pt chains at 77 K, it is important to compare the probability distribution for the nearest-neighbor separation of DE-DE, B-B, and DE-B adsorption site pairs. Interestingly, the characteristic long-range repulsive interaction is observed for all combinations, i.e., DE-DE, B-B, and DE-B. As referred to above, we emphasize that we have also examined the interaction between adsorbed CO molecules in adjacent Pt chains. Our analysis reveals that this interaction is very weak if existent at all.

We emphasize that the range of the repulsive interaction between adsorbed CO molecules is unusually large compared to the interactions between CO molecules on monocrystalline Pt surfaces. A *qualitative* explanation of this remarkable observation can be given by using the Blyholder adsorption model.^{16,20,25} As mentioned before, this model basically consists of two parts. The second part, in which electrons are backdonated from the metal $d\pi$ orbital into the LUMO of CO, most often is larger than the first part. Hence, the net result is that the electron density of the metal reduces. However, dipole-dipole interactions alone are insufficient to explain the unusually long range of the interaction since they decay very rapidly. For our Pt/Ge(001) system we expect that in the vicinity of an adsorbed CO molecule there is a zone in which the electron density is significantly reduced. Thus, within a certain range the electron density of the neighboring Pt dimers is depleted. It should be noted that we assume that the electrons predominantly come from the Pt chain and not from the underlying substrate. Compared to, e.g., Pt(111), the density of free electrons is strongly reduced and thus screening effects are much less effective leading to an enhanced lateral length scale for repulsion.

Due to the asymmetric donation/backdonation model, the adsorption of a CO molecule will lead to small dipole. Since all the dipoles are aligned perpendicular to the surface, an adsorbed CO molecule also hinders the adsorption of another CO molecule in its direct proximity.

IV. SUMMARY

In summary, we have studied the adsorption of CO molecules on a Pt modified Ge(001) surface at 77 K. There are two different adsorption sites: a long-bridge adsorption site (DE) and a short-bridge or on-top adsorption site on the buckled Pt dimers. Irrespective of the exact nature of the adsorption site, the CO molecules adsorbed on the same Pt chain repel each other with the same characteristic length scale. We suggest that this repulsive interaction is comprised of a repulsive dipole-dipole term and strain-mediated term.

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