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Local modification of the surface state properties at dilute coverages: CO/Cu(111)

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We follow the diffusion of CO molecules on Cu(111) by time-lapsed low-temperature scanning tunneling microscopy. The diffusivity of individual CO molecules oscillates with the distance to its nearest neighbor due to the long-range interaction mediated by the surface state electrons. The markedly different wavelengths of the oscillation at a coverage of 0.6% ML as compared to the one at 6% ML coverage correspond to two different wavelengths of the surface state electrons, consistent with a shift of the surface state by 340 meV. This surprisingly large shift as compared to results of averaging methods suggests a local modification of the surface state properties.

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Surface states situated in the large sp-band gap of the projected bulk band structure along the Γ-L line on fcc(111) surfaces of noble metals [1] govern a variety of surface processes including epitaxial growth [2], surface chemistry [3,4], adatom island decay [5], formation of adatom superlattices [6–10], and coupling between defects [11]. Adsorption of alkali metals, rare gases, or organic molecules alter the surface state's electronic structure resulting in a so-called interface state [12–15]. The thus created interface state's origin is the same as the surface state, the abrupt change of the potential perpendicular to the interface [16]. The surface potential barrier is however steeper in the case of a dielectric layer than in the case of an interface to vacuum, leading to an upshift in energy. The dispersion relation of interface states was characterized theoretically and experimentally for dense islands, monolayers, and bilayers of a number of insulating, dielectric material, e.g., Xe [13,14,17,18], MgO [19], NaCl [20–22], and organic monolayer films, mainly of PTCDA (3,4,9,10-perylenetetracarboxylic-acid-dianhydride) derived molecules [16,23–25]. For PTCDA derived molecules, the energy difference between the initial surface state and the resulting interface state varies with film thickness, adsorption distance, molecule size, and molecule geometry, at unchanged effective mass [26,27]. Further investigated metal-organic interfaces showed similar behavior as pentacene/Cu(110) [28], adenine/Ag(111) [29], ferrocene/Cu(111) [30], thiophenol/Cu(111) [31]. The energy change has also been found to be accompanied by a change in effective mass in some cases [31], in particular for different architectures of porous networks on Cu(111) [32] and NaCl islands of different density on Ag(111) [33]. All studies addressed the limit of extended films or densely packed ordered islands. What has not yet been investigated to our knowledge is how local perturbations of the potential at dilute coverage influence the surface/interface state properties.

On the other hand, the electrons populating the surface state on several fcc(111) surfaces form a confined two-dimensional electron gas, a medium that enables transport of signals over larger distances. It can thus be used to address molecules at some distance from the stimulus [34] or an ensemble of molecules simultaneously with a single stimulus [35]. The most investigated issue of this property is the distance-dependent modification of the adsorbate's diffusion potential Φ by another adsorbate at some nanometer distance [36–38] as revealed from the analysis of nearest neighbor distance distributions obtained from scanning tunneling microscopy (STM) images [7,10,39–42] and more recently by time-lapsed STM [43–45]. The wavelength of the oscillation is directly related to the bottom of the surface state making it a good measure for the energetic position of the surface/interface state. In all studies so far, the wavelength of the oscillation reflected the properties of the respective surface state of the pristine surface.

In this paper, we determine the distant-dependent energy barrier for diffusion of CO molecules on Cu(111) via time-lapsed scanning tunneling microscopy at two different coverages. At both coverages this energy oscillates with distance. At 0.6% ML, the oscillation wavelength reflects the properties of the surface state of the pristine surface. However, already at a coverage of 6% ML, the oscillation wavelength is changed by 30% corresponding to a shift of the surface state by approximately 350 meV. This large shift at dilute coverages is consistent with an enhanced local coverage and suggests a substantial variation in surface/interface state properties over surfaces with coverage fluctuations.

I. EXPERIMENTAL METHODS

The experiments were performed with a home-built low temperature STM in UHV (base pressure $\leqslant 2\times10^{-10}$ mbar) [46]. Cu(111) is cleaned by standard sputtering and annealing cycles. After cleaning, 0.6% or 6% ML of CO is deposited on the sample at 22 K. The sample is then transferred into the STM. Diffusion of the molecules is induced by *in situ* heating and imaging of the same spot of the surface at regular time intervals leading to so-called STM movies. Measurements are

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performed between 30 and 38 K at 0.6% ML. We concentrate for the coverage of 6% ML on 32 K, because we do not expect that the prefactor for diffusion is coverage dependent.

Special care is taken to determine the temperature at the sample exactly by calibrating the temperature diodes used to high precision and by determining the temperature drop between the position of the Si diode and the sample. For details see Ref. [47]. A careful stabilization of the temperature reduces the drift during the measurement to negligible values. The influence of the tip on the molecule motion is checked by recording movies at equivalent image acquisition time with double and triple time interval as described in detail in Refs. [48,49]. Diffusivities derived for these different data sets are identical within the experimental error bars.

The movies are analyzed semiautomatically using a program written in the program language LabView. The center-of-mass of the CO molecules is determined by fitting a two-dimensional Gaussian function. After a position of a molecule was determined, also the distance and type of its neighboring objects are recorded.

The motion of individual molecules is followed by comparison of the positions of all objects in subsequent images of the movie. The path of each molecule is overlaid over the movie during a second run, so that the user can confirm that the tracking procedure was correct; for an example see the online material.

II. RESULTS

To set the stage for the diffusion measurements, we first characterize the CO molecules geometrically at the two investigated coverages. Figure 1(a) shows a Cu(111) surface at a CO coverage of $\rho_{CO} = 0.6\%$ ML. Each CO molecule is imaged as an apparent depression corresponding to a molecule that is adsorbed with its molecular axis perpendicular to the surface in an on-top site [50,51]. Fitting a Gaussian function reveals an apparent depth of $z_0 = (28.8 \pm 0.2)$ pm at a width of $\sigma_0 = (0.23 \pm 0.01)$ nm [Fig. 1(c)]. The surface state electrons that mediate the long-range interaction are visible on such images as circular standing waves around the molecules.

Regions of different local coverage are observed at the higher coverage of $\rho_{CO} = 6\%$ ML. The geometrical parameters are preserved in regions of lower local coverage [e.g., lower red square in Fig. 1(b)]. However, in regions of larger local coverage, for instance in the lower white square in Fig. 1(c), the apparent diameter of the molecules seems to be slightly smaller. This impression is, however, not reflected in the line scans [Fig. 1(d)] as exemplified for two randomly chosen cases in Fig. 1(d). The red line scan is representative for lower coverage as for instance marked by the upper red square, and the black/white line scan is representative for the higher coverage as for instance marked by the lower red square. The line scans show that the absolute heights of the line profiles of CO molecules and not their half width differs in dependence of the local coverage. This is an effect of the standing waves caused by scattering of the surface state electrons of Cu(111) at the CO molecules. Such scattered electrons form standing waves that lead to local variations in the electronic density of states. As STM images this local density-of-states (LDOS), an overlap of high densities from standing wave patterns from different molecules influences the measured apparent height. This can be best observed at the lower coverage [Fig. 1(a)]. The first maximum of the resulting standing wave pattern is largest. If two maxima overlap, constructive interference leads to a substantial increase in apparent height [see arrow in Fig. 1(a)]. In regions of large CO density the accumulation of charge leads to an apparent larger background [Figs. 1(b) and 1(d)] and thus the CO molecule's depression seems to be lifted up as compared to other regions of the surface.

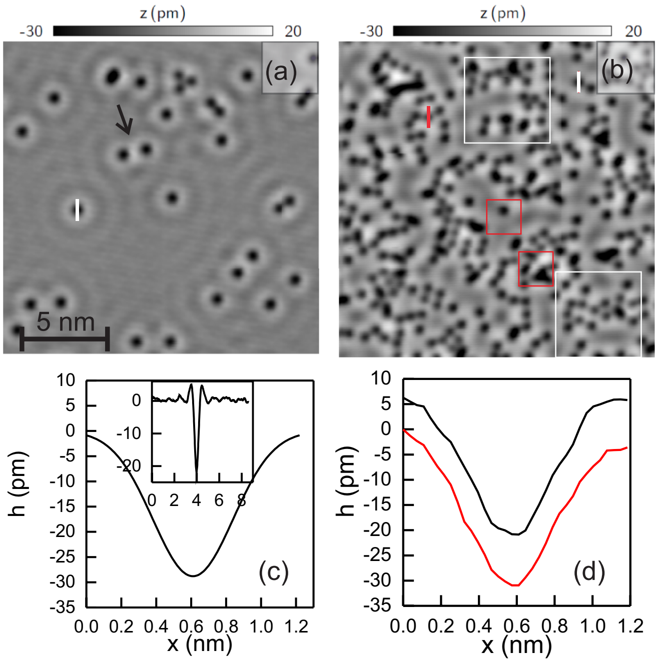

FIG. 1. STM image of CO molecules on Cu(111) at a coverage of (a) 0.6% ML ($I = 44$ pA, $V = 200$ mV, $T = 32.5$ K); arrow points to two molecules with constructively interfering standing wave pattern (see text) (b) 6% ML ($I = 44$ pA, $V = 200$ mV, $T = 31.8$ K); squares mark regions of different local coverage (see text). (c),(d) Height profiles of individual CO molecules as marked in (a),(b); inset in (c) across a larger range.

After having characterized the CO molecules, we now set distinct temperatures and follow the motion of the CO molecules at each temperature for some hours to days. Figures 2(a) and 2(b) show snapshots of such movies recorded at 32 K for the two investigated coverages. At the lower coverage, only molecules that are close to each other change position between the images [Fig. 2(a)]. At the higher coverage, many more molecules are at this closer distance. Indeed, the number of molecules that change position between the images increases substantially [Fig. 2(b)].

In order to quantify this observation, we now determine the distances that individual molecules diffused between subsequent images as shown in Fig. 3 for the higher coverage of 6% ML as 2D distance histograms. The histograms reveal that the CO molecules diffuse randomly on a hexagonal lattice, consistent with motion between on-top sites, on which their position is thus directly mapped. The distance dependent histograms confirm that the motion is largest for the distance range up to 1 nm, smaller for distances between 1 nm and 2 nm, and smallest for the distance range of 2 nm to 3 nm. For the

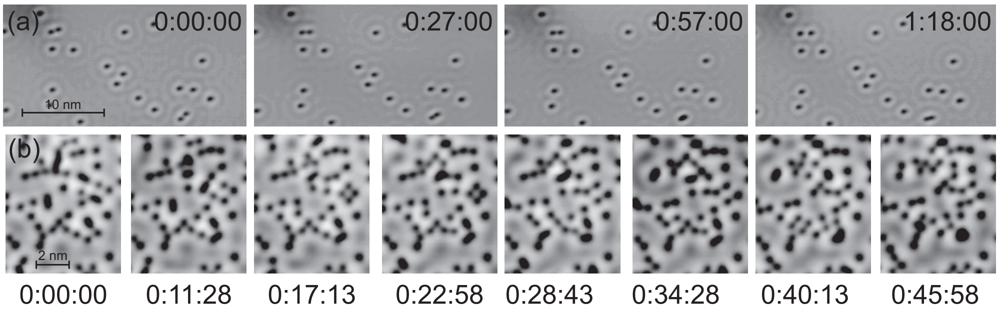

FIG. 2. Snapshot of STM movies at 32 K; indicated times in h:min:s at a coverage of (a) 0.6% ML, 228 mV, 51 pA, (b) 6% ML, 200 mV, 44 pA.

lower coverage, we have shown before that this dependence is in fact oscillatory [44].

To set the stage for a quantitative discussion of this qualitatively observed distance and coverage dependence, we shortly recapitulate the here relevant results that we achieved for the lower coverage of 0.6% ML before [44]. The diffusivity of the CO molecules were determined from the data via the Einstein relation and then plotted in an Arrhenius plot giving an average diffusion energy of CO on Cu(111) of $E_{\mathrm{Dave}} = (98.4 \pm 0.5)$ meV [44]. In order to determine distance-dependent energy barriers, the data was divided into subsets smaller than the ones shown in Fig. 3 corresponding to different nearest neighbor distances. Arrhenius plots for each distance delivered distance dependent energy barriers that change in an oscillatory way, as partly reproduced in Fig. 4(a) from Ref. [44]. The energy barrier oscillation with distance is consistent with theory [36,37].

For two interacting adsorbates with distance d and well separated from all other adsorbates, such a change in interaction energy is asymptotically given by $\Delta E_{\mathrm{pair}}(d)$ [36,37]:

$$\Delta E_{\mathrm{pair}}(d) = -\frac{4}{\pi^2}\epsilon_F A(r,\varphi_F)\frac{\sin(2k_F d + 2\varphi_F)}{(k_F d)^2}. \qquad (1)$$

Here, ϵ_F, k_F, and φ_F are the bottom of the surface state band, the Fermi wave vector, and the scattering phase of the surface state electrons in this band, respectively. For a perfect scatterer with phase shift $\varphi \approx \pi/2$ and reflectivity $r = 1$ the usually complex prefactor simplifies to $A = \sin^2\varphi_F$.

Fitting $\Delta E_D = \alpha_{\mathrm{pair}} \cdot \Delta E_{\mathrm{pair}}$ [see Eq. (1)] with α_{pair} an empirical fitting parameter yielded $k_F = (2.1 \pm 0.1)\ \mathrm{nm}^{-1}$, $\varphi_F = (0.6 \pm 0.1)\pi$, and $\alpha_{\mathrm{pair}} = 0.03 \pm 0.01$ for the lower coverage of 0.6% ML [53]. On Cu(111), the surface state band is parabolic with an onset energy of $\epsilon_F = -(440 \pm 10)$ meV and an effective electron mass of $m^* = (0.38 \pm 0.02)m_e$ [52]. This yields a Fermi wave vector of $k_F = \sqrt{2m^*\epsilon_F}/\hbar = 2.1\ \mathrm{nm}^{-1}$. Thus, the value of the Fermi wave vector k_F for the lower coverage is the one expected for Cu(111). Furthermore, φ_F is in good agreement with the value expected for a perfect scatterer.

Having recapitulated results for low coverage, we now explore changes to the oscillatory distribution at higher coverage. Following the same procedure, we determine the distance d of each molecule to its nearest neighbor (NN) and subsequently the diffusion constant for different NN distances via the Einstein relation $\langle \Delta x^2 \rangle = 2D\Delta t$. Distances of the nearest neighbors larger than 1 nm^2 are too rare at this higher coverage to yield reasonable error bars. At lower distances, the interaction energy oscillates also at the higher coverage [Fig. 4(b)]. However, both, the first minimum and maximum reside at smaller distance. Indeed, fitting Eq. (1), using the scattering phase $\phi_F = 0.5\pi$ for the perfect scatterer and the amplitude factor $\alpha_{\mathrm{pair}} = 0.03$ determined before [44], we obtain a wave vector of $k_F = (2.8 \pm 0.3)/\mathrm{nm}$ [54].

The wave vector at the higher coverage is considerably larger than the one at lower coverage. This larger wave vector corresponds to a shift of the energy of the surface state by (340 ± 150) meV.

Photoelectron spectra of Cu(111) showed a linear shift of the surface state upon CO adsorption with 1.5 eV/ML up to a coverage of 0.45 ML [55]. The gradual shift, proportional to the density of adsorbed molecules, can be understood by realizing that nonmolecule covered regions between the molecules lead to a leakage of the state's wave function into the vacuum [25]. The shift is linear because of the dependence of the radius r

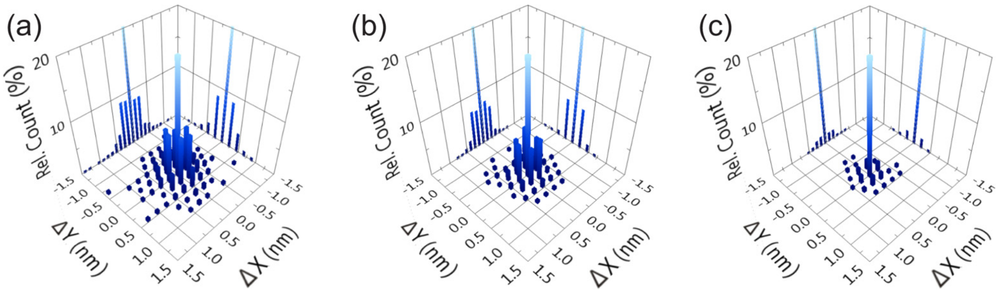

FIG. 3. Two-dimensional histogram of CO motion at 6% ML for molecules with the next nearest neighbor at (a) up to 1 nm, (b) 1 nm to 2 nm, (c) 2 nm to 3 nm.

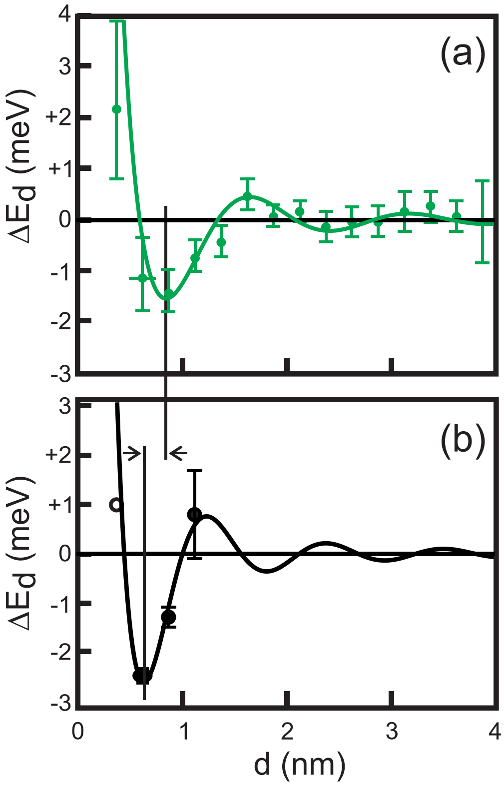

FIG. 4. Change in diffusion barrier ΔE_D with respect to $E_{\text{Dave}} =$ (98.4 ± 0.5) meV [44] versus distance d to next nearest neighbor for a coverage of (a) 0.6% ML, (b) 6% ML; vertical lines mark positions of first minimum.

of the bare surface around an adsorbate on the coverage θ. The surface state electrons scatter in an area πr^2 around an adsorbate. The radius r scales with $1/\sqrt{\theta}$ for random growth. Thus, the energy of the surface state scales with θ [55]. For the coverage of 6% ML investigated here, the corresponding change in work function would be only ≈70 meV and thus the observed shift cannot simply reflect a change in work function [56]. Vice versa, a shift by 340 meV would correspond to a coverage of 23% ML, four times the experimental coverage.

On the other hand, 2PPE showed for full monolayer adsorption that the amount of shift induced by carbon containing molecules depends on adsorption distance [16]. Extrapolating the data for graphene and PTCDA related molecules to the calculated C-Cu adsorption length in an on-top site of 0.185 nm [44] yields an energy shift by 2.14 eV at full monolayer coverage and thus 130 meV at 6% ML, a value still much lower than observed here, or vice versa, a shift by 340 meV would correspond to a coverage of 16% ML according to this reasoning, three times the experimental coverage.

The large value of the shift is thus surprising at such low coverage. It means that even quite small amounts of randomly distributed CO molecules strongly modify the Cu(111) surface potential much more than expected from the measured global shift in work function. Note that the local coverage varies considerably; for the two white squares of 5 nm × 5 nm in Fig. 1(b) by 50% and for the two red squares of 2 nm × 2 nm by an order of magnitude. Our data thus suggests that this variation in local coverage is accompanied by a local variation in work function. The wavelength should be characteristic for the local coverage, which depends on distance and not for the global one. Indeed, the range of coverage determined above from the observed shift between 16 and 23% ML correspond to a nearest neighbor distance of 0.64 nm to 0.51 nm for equally spaced molecules, in the range of the distances where we observe the shift of the oscillation extrema. This implies that the shift of the surface state measured for nearest neighbors in the region up to 1 m is not present in the more dilute regions, where, indeed, we do not observe a motion of the molecules in Fig. 2. In the region of molecules with close nearest neighbors, the local coverage thus determines the shift of the surface state. Our interpretation is corroborated by an order of magnitude increase in line width in the photoemission line of 2PPE spectra upon shift. Our data suggests that this broad line width results from the superposition of different positions of the surface state at different parts of the surface.

III. CONCLUSION

We have shown a distinct variation in surface state properties on a nanometer length scale. Similar decreases in wavelength should occur on other fcc(111) metals with an occupied surface state. Our study suggests that not only adsorbate-adsorbate interactions have to be considered already at dilute coverage, but also the subtle interplay between the adsorbate and the surface. All named processes that are governed by the surface state have to take these changes into account at much lower coverages than hitherto assumed.

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[1] A. Goldmann, V. Dose, and G. Borstel, Phys. Rev. B **32**, 1971 (1985).
[2] N. Memmel and E. Bertel, Phys. Rev. Lett. **75**, 485 (1995).
[3] A. G. Borisov, A. K. Kazansky, and J. P. Gauyacq, Phys. Rev. Lett. **80**, 1996 (1998).
[4] L. Guillemot and V. A. Esaulov, Phys. Rev. Lett. **82**, 4552 (1999).
[5] K. Morgenstern, E. Laegsgaard, and F. Besenbacher, Phys. Rev. Lett. **94**, 166104 (2005).
[6] S. J. Stranick, M. M. Kamna, and P. S. Weiss, Science **266**, 99 (1994).
[7] J. Repp, F. Moresco, G. Meyer, K.-H. Rieder, P. Hyldgaard, and M. Persson, Phys. Rev. Lett. **85**, 2981 (2000).
[8] H. Y. Lin, Y. P. Chiu, L. W. Huang, Y. W. Chen, T. Y. Fu, C. S. Chang, and T. T. Tsong, Phys. Rev. Lett. **94**, 136101 (2005).
[9] T. Mitsui, M. K. Rose, E. Fomin, D. F. Ogletree, and M. Salmeron, Phys. Rev. Lett. **94**, 036101 (2005).

[10] M. Mehlhorn, V. Simic-Milosevic, S. Jaksch, P. Scheier, and K. Morgenstern, Surf. Sci. **604**, 1698 (2010).

[11] K. Seufert, W. Auwärter, F. J. G. de Abajo, D. Ecija, S. Vijayaraghavan, S. Joshi, and J. V. Barth, Nano Lett. **13**, 6130 (2013).

[12] H. P. Bonzel, Surf. Sci. Rep. **8**, 43 (1988).

[13] J.-Y. Park, U. D. Ham, S.-J. Kahng, Y. Kuk, K. Miyake, K. Hata, and H. Shigekawa, Phys. Rev. B **62**, R16341 (2000).

[14] H. Hövel, G. Grimm, and B. Reihl, Surf. Sci. **477**, 43 (2001).

[15] F. Forster, G. Nicolay, F. Reinert, D. Ehm, S. Schmidt, and S. Hüfner, Surf. Sci. **532-535**, 160 (2003).

[16] M. Marks, A. Schöll, and U. Höfer, J. El. Spect. Rel. Phen. **195**, 263 (2014).

[17] M. Wolf, E. Knoesel, and T. Hertel, Phys. Rev. B **54**, R5295 (1996).

[18] H. F. Bowen and B. Space, J. Chem. Phys. **107**, 1922 (1997).

[19] Y. Pan, S. Benedetti, N. Nilius, and H.-J. Freund, Phys. Rev. B **84**, 075456 (2011).

[20] J. Repp, G. Meyer, and K. H. Rieder, Phys. Rev. Lett. **92**, 036803 (2004).

[21] F. Matthaei, S.-C. Heidorn, K. Boom, C. Bertram, A. Safiei, J. Henzl, and K. Morgenstern, J. Phys.: Condens. Matter **24**, 354006 (2012).

[22] S.-C. Heidorn, C. Bertram, P. Cabrera-Sanfelix, and K. Morgenstern, ACS Nano **9**, 3572 (2015).

[23] C. H. Schwalb, S. Sachs, M. Marks, A. Schöll, F. Reinert, E. Umbach, and U. Höfer, Phys. Rev. Lett. **101**, 146801 (2008).

[24] M. Marks, N. L. Zaitsev, B. Schmidt, C. H. Schwalb, A. Schöll, I. A. Nechaev, P. M. Echenique, E. V. Chulkov, and U. Höfer, Phys. Rev. B **84**, 081301 (2011).

[25] P. Jakob, N. L. Zaitsev, A. Namgalies, R. Tonner, I. A. Nechaev, F. S. Tautz, U. Höfer, and D. Sanchez-Portal, Phys. Rev. B **94**, 125436 (2016).

[26] N. L. Zaitsev, I. A. Nechaev, P. M. Echenique, and E. V. Chulkov, Phys. Rev. B **85**, 115301 (2012).

[27] N. Armbrust, F. Schiller, J. Güdde, and U. Höfer, Sci. Rep. **7**, 46561 (2017).

[28] A. Scheybal, K. Müller, R. Bertschinger, M. Wahl, A. Bendounan, P. Aebi, and T. A. Jung, Phys. Rev. B **79**, 115406 (2009).

[29] K. M. Andrews and T. P. Pearl, J. Chem. Phys. **132**, 214701 (2010).

[30] B. W. Heinrich, L. Limot, M. V. Rastei, C. Iacovita, J. P. Bucher, D. M. Djimbi, C. Massobrio, and M. Boero, Phys. Rev. Lett. **107**, 216801 (2011).

[31] S.-Y. Hong, P.-C. Yeh, J. I. Dadap, and R. M. Osgood Jr., ACS Nano **6**, 10622 (2012).

[32] S. Wang, W. Wang, L. Z. Tan, X. G. Li, Z. Shi, G. Kuang, P. N. Liu, S. G. Louie, and N. Lin, Phys. Rev. B **88**, 245430 (2013).

[33] S.-C. Heidorn, A. Sabellek, and K. Morgenstern, Nano Lett. **14**, 13 (2014).

[34] H. Gawronski, J. Carrasco, A. Michaelides, and K. Morgenstern, Phys. Rev. Lett. **101**, 136102 (2008).

[35] V. Schendel, B. Borca, I. Pentagov, T. Michnowicz, U. Kraft, H. Klauk, P. Wahl, U. Schlickum, and K. Kern, Nano Lett. **16**, 93 (2016).

[36] P. Hyldgaard and M. Persson, J. Phys.: Condens. Matter **12**, L13 (2000).

[37] P. Hyldgaard, J. Phys.: Condens. Matter **24**, 424219 (2012).

[38] P. Han and P. S. Weiss, Surf. Sci. Rep. **67**, 19 (2012).

[39] E. Wahlström, I. Ekvall, H. Olin, and L. Walldén, Appl. Phys. A **66**, S1107 (1998).

[40] N. Knorr, H. Brune, M. Epple, A. Hirstein, M. A. Schneider, and K. Kern, Phys. Rev. B **65**, 115420 (2002).

[41] K. Morgenstern, K.-F. Braun, and K.-H. Rieder, Phys. Rev. Lett. **93**, 056102 (2004).

[42] K. Morgenstern and K.-H. Rieder, New J. Phys. **7**, 139 (2005).

[43] K. L. Wong, B. V. Rao, G. Pawin, E. Ulin-Avila, and L. Bartels, J. Chem. Phys. **123**, 201102 (2005).

[44] C. Zaum, K. M. Meyer-auf-der-Heide, M. Mehlhorn, S. McDonough, W. F. Schneider, and K. Morgenstern, Phys. Rev. Lett. **114**, 146104 (2015).

[45] C. Zaum and K. Morgenstern, Nano Lett. **16**, 3001 (2016).

[46] M. Mehlhorn, H. Gawronski, L. Nedelmann, A. Grujic, and K. Morgenstern, Rev. Sci. Instrum. **78**, 033905 (2007).

[47] C. Zaum, C. Bertram, K. M. Meyer auf der Heide, M. Mehlhorn, and K. Morgenstern, Rev. Sci. Instr. **87**, 053902 (2016).

[48] K. Morgenstern, G. Rosenfeld, B. Poelsema, and G. Comsa, Surf. Sci. **352-354**, 956 (1996).

[49] K. Morgenstern, G. Rosenfeld, G. Comsa, M. R. Sørensen, B. Hammer, E. Lægsgaard, and F. Besenbacher, Phys. Rev. B **63**, 045412 (2001).

[50] R. Raval, S. F. Parker, M. E. Pemble, P. Hollins, J. Pritchard, and M. A. Chesters, Surf. Sci. **203**, 353 (1988).

[51] G. Meyer, L. Bartels, S. Zöphel, and K.-H. Rieder, Appl. Phys. A **68**, 125 (1999).

[52] M. F. Crommie, C. P. Lutz, and D. M. Eigler, Nature (London) **363**, 524 (1993).

[53] The low value of α_{pair}, only 3% of the theoretically expected value, reflects the fact that the measured oscillation in energy underestimates the real one [44]. Two points were shown to be responsible for the discrepancy between the real interaction strength and the measured one [44]: the discretization induced by the hexagonal lattice and a minute averaging of several distances as is unavoidable in any experiment [cf. Fig. 4(a)]. Thus, the apparent 2 meV oscillation corresponds to a pair interaction that oscillates by at least 25 meV.

[54] An earlier study of 1% ML Cu on Cu yielded $k_F \approx 2.1\ \text{nm}^{-1}$, $\phi_F \approx 0.30\pi$ [7]. However, it is unlikely that two different phases exist for the scattering of an electron on the same particle. Our increased statistics and very careful calibration procedure explained elsewhere [47] is able to disentangle the two free parameters, phase and wave vector.

[55] F. Baumberger, T. Greber, B. Delley, and J. Osterwalder, Phys. Rev. Lett. **88**, 237601 (2002).

[56] Note that this kind of original explanation [57] has been disproved [14].

[57] S. A. Lindgren, J. Paul, and L. Wallden, Surf. Sci. **117**, 426 (1982).