

Long-Range Electronic Interactions at a High Temperature: Bromine Adatom Islands on Cu(111)

Sanjini U. Nanayakkara, E. Charles H. Sykes, Luis C. Fernández-Torres, Meaghan M. Blake, and Paul S. Weiss*

*Departments of Chemistry and Physics, The Pennsylvania State University,
104 Davey Laboratory, University Park, Pennsylvania, 16802-6300 USA*

(Received 4 January 2006; published 17 May 2007)

Long-range electronic interactions between Br adatom islands, which are formed at ~ 600 K, on Cu(111) are mediated by substrate surface-state electrons at that elevated temperature. Using scanning tunneling microscopy at 4 K, we have quantified nearest neighbor island separations and found favored spacings to be half-multiples of the Fermi wavelength of Cu(111). The strong interaction potential and decay length of the interisland interactions are discussed in terms of the interaction of Br with the substrate surface state.

DOI: [10.1103/PhysRevLett.98.206108](https://doi.org/10.1103/PhysRevLett.98.206108)

PACS numbers: 68.35.Ja, 68.37.Ef, 68.43.-h, 73.20.At

Adsorbate-adsorbate interactions on surfaces are critical to surface phenomena such as catalysis and thin film growth. Short-range order between adsorbates can be achieved by direct interactions, typically between 1 and 5 Å, via chemical bonds or through charges and/or dipoles. Interactions at larger separations can occur when the surface is physically or electronically perturbed as a result of adsorption and/or surface stress, which enables adsorbates to interact via the substrate [1–5]. Here, we present a quantitative study of the role of the surface-state electrons in mediating long-range, indirect interactions between aggregates of adatoms at catalytically relevant temperatures.

Substrate-mediated long-range interactions were first hypothesized by Koutecký [2]. Theoretical analyses [6,7] and experimental observations soon followed [8,9]. Lau and Kohn predicted that long-range interactions mediated by a partially filled surface-state band lead to an oscillatory interaction potential with a period of half the Fermi wavelength ($\lambda_F/2$) of the substrate [10].

Surface-state electrons of close-packed (111) surfaces of noble metals are known to behave as two-dimensional (2D) nearly free electron gases [11–13]. Substrate steps, defects, and adsorbates on such surfaces act as barriers that scatter surface-state electrons and create standing waves, which can mediate interactions between adsorbates [1–5,14,15]. These spatial oscillations in the local density of states (LDOS) can be observed directly using scanning tunneling microscopy (STM) [11,16,17]. A quantitative analysis of long-range interaction energies mediated by a 2D electron gas between single adatoms was reported by Repp *et al.*, who investigated Cu/Cu(111) at 9–12 K using STM [18]. Knorr *et al.* then studied three different systems, Cu/Cu(111), Co/Cu(111), and Co/Ag(111) [19]. These long-range interactions were not sensitive to the adatom identity, but were dependent on the substrate surface-state electrons [19]. Morgenstern *et al.* studied the role of the surface state in the interactions and motion of Cu adatoms and dimers on Ag(111) [20]. We have determined the effects of the perturbed LDOS due to interfering surface-state electrons scattered from step edges on the adsorption of CO on Ag(111) [21]. Here, we extend the understanding

of surface-state-mediated indirect interactions from single adsorbates to larger aggregates of adatoms at catalytically relevant temperatures.

We present a quantitative study of the long-range interactions between Br adatom islands on Cu(111). The Br adatom islands were created by ramping the substrate temperature up to 600 K after a 200 L exposure to bromobenzene (C_6H_5Br) at 293 K [22]. Upon exposure to the Cu surface at 293 K, C_6H_5Br dissociated to form phenyl (C_6H_5) intermediates and Br adatoms, after which the phenyl intermediates coupled to form biphenyl ($C_6H_5-C_6H_5$) molecules [Fig. 1(a)] [23,24]. By annealing up to 600 K, the biphenyl molecules desorbed at ~ 390 K [23,24], leaving behind only Br adatoms [22–24]. During annealing, Br adatoms that were randomly distributed and immobile at 293 K [Fig. 1(a)] became mobile and aggregated to form islands [Fig. 1(b)], at ~ 600 K [22,25,26]. We used scanning tunneling spectroscopy to verify the identity of Br adatoms before and after annealing [Fig. 1(c)]. The spatially varying interaction potential between islands was determined by evaluating the distance distribution between the Br islands from a series of non-overlapping STM images recorded at 4 K. We found that the interaction potential is oscillatory with energy minima observed at ca. 12, 26, 41, and 56 Å. This corresponds to a 15 Å period, which is $\lambda_F/2$ for Cu(111). We conclude that the surface state is essential in mediating interactions between adsorbates at catalytically relevant temperatures.

All experiments were performed using a custom-built, cryogenic, extreme high vacuum STM, described elsewhere [27]. The Cu(111) single crystal (MaTeck, Jülich, Germany) was cleaned by cycles of Ar ion sputtering and annealing [22]. All STM images shown were recorded at 4 K in constant-current mode. Tunneling spectra in differential conductance mode were recorded using a lock-in amplifier (model SR850, Stanford Research Systems) by modulating the bias voltage with an ac amplitude of 8 mV (rms), 1000 Hz and recorded with a 30-ms time constant. Spectra were acquired over randomly distributed and isolated Br adatoms [Fig. 1(a), imaged as depressions] and Br adatom islands [Fig. 1(b)] and were compared to spectra

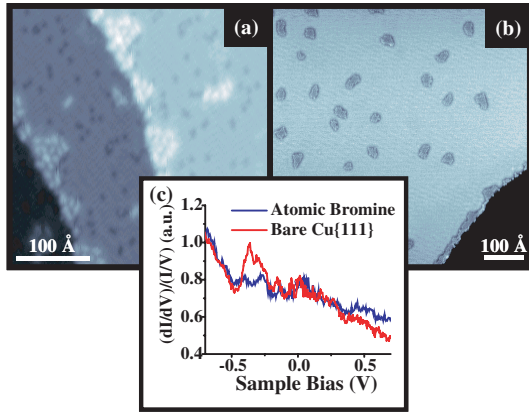


FIG. 1 (color). Scanning tunneling microscopy images before and after Br adatom island formation recorded at 4 K. (a) Biphenyl molecules (protrusions, along the step edges) and Br adatoms (depressions, isolated and randomly distributed over the terraces) prior to the annealing step ($340 \text{ \AA} \times 340 \text{ \AA}$; $I_t = 10 \text{ pA}$; $V_{\text{sample}} = -0.75 \text{ V}$). (b) After annealing up to 600 K, the biphenyl molecules desorbed and the Br adatoms aggregated to form islands ($630 \text{ \AA} \times 630 \text{ \AA}$; $I_t = 12 \text{ pA}$; $V_{\text{sample}} = -0.75 \text{ V}$). Inset: Differential conductance spectra were recorded as described in the text. Spectra acquired over the bare Cu surface (red) and Br adatoms (blue) are shown. Note that the surface state at -0.4 eV is quenched locally by Br adatoms.

acquired over the bare Cu surface [Fig. 1(c)] [22]. The Cu(111) surface-state band edge observed at 0.4 eV below the Fermi level [red line, Fig. 1(c)], the signature for identifying the bare Cu surface, was not observed over the Br adatoms [blue line, Fig. 1(c)] in either case, consistent with halogens, which quench the surface state of Cu(111) [28]. Three STM images of the Cu(111) surface with 0.03 monolayer coverage of Br adatom islands are shown in Figs. 2(a)–2(c). The Br adatoms within all the islands formed $(\sqrt{3} \times \sqrt{3})R30^\circ$ structures [Figs. 2(a) and 2(b)] on Cu(111), as previously observed for a submonolayer of Br by low energy electron diffraction [29]. As shown in Fig. 2(a), Br adatom islands were distributed over terraces and along the tops of step edges.

Interference patterns (standing waves) created by scattering of the surface state from the islands are visible in the STM image shown in Fig. 2(c), which was recorded at a sample bias close to the Fermi level (-50 mV), and indicated surface-state-mediated interactions between these islands (the Br adatom islands appeared as depressions and the atoms were not resolved in this image due to its large size). To quantify the long-range interactions between the Br adatom islands, we evaluated over 3000 interisland separations from more than 200 nonoverlapping STM images and plotted a histogram of these separations [Fig. 2(d)].

We used an analysis similar to that used for Tsong’s field ion microscopy experiments [8]. The interaction potential $E(r)$ between the Br islands was determined as

$$E(r) = -k_B T \ln[(g(r))], \quad (1)$$

where T is the temperature at which the islands were

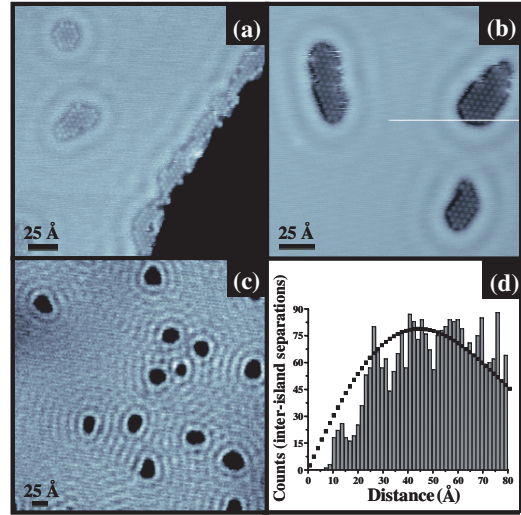


FIG. 2 (color online). Scanning tunneling microscopy images of Br adatom islands on Cu(111), recorded at 4 K. (a) Br adatom islands ($211 \text{ \AA} \times 211 \text{ \AA}$; $I_t = 20 \text{ pA}$; $V_{\text{sample}} = -0.2 \text{ V}$) on Cu terraces and decorating step edges. (b) Br adatom structures of $(\sqrt{3} \times \sqrt{3})R30^\circ$ within the islands ($176 \text{ \AA} \times 176 \text{ \AA}$; $I_t = 20 \text{ pA}$; $V_{\text{sample}} = -0.2 \text{ V}$). (c) Large-scale STM image recorded at a bias close to the Fermi level ($420 \text{ \AA} \times 420 \text{ \AA}$; $I_t = 10 \text{ pA}$; $V_{\text{sample}} = -50 \text{ mV}$) illustrating the interference patterns of the standing waves created by scattering of the Cu surface-state electrons from islands. (d) Histogram of separations between Br islands determined from a series of ~ 200 nonoverlapping STM images recorded at 4 K. The dotted line illustrates the expected distribution in the absence of any interisland interactions.

formed, k_B is the Boltzmann constant, and $g(r)$ is the pair correlation function. The pair correlation function was extracted by dividing the experimental pair distribution function [histogram in Fig. 2(d)] by the theoretical function for similar noninteracting species on the surface [dotted line in Fig. 2(d)] [8]. We measured only the closest distance between the edges of the islands that had no other islands between, thus considering only two-body interactions. The theoretical function for noninteracting islands was derived as by Knorr *et al.* [19]. The interaction potential between Br adatom islands, $E(r)$, plotted as a function of distance between the islands r (Fig. 3 inset).

We analyzed the interaction energy by two methods. First, we overlaid the experimental interaction energy plot [solid line, Fig. 3 inset] with a theoretical energy plot (dashed line in Fig. 3) adapted from Hyldgaard and Persson [30]. In comparison with the theoretical energy plot, we observed potential energy minima at 12 , 26 , 41 , and 56 \AA (solid line in Fig. 3). The first potential energy minimum at 12 \AA corresponds to the first favorable distance between the islands, and the following minima are observed at intervals of $\sim 15 \text{ \AA}$. This interval corresponds to $\lambda_F/2$ for Cu(111), indicating that the surface state plays an important role in mediating the lateral distances between the Br islands. Additionally, the amplitude of the interaction strength decays as $1/r^2$ with distance r [10].

The position of the first energy minimum determines the scattering phase shift of the Br adatom islands. Our first minimum observed at ~ 12 Å, indicative of a phase shift of $\pi/2$, is in good agreement with the values for a typical blackbody scatterer [18,19]. However, at distances shorter than the first minimum, we observe a divergence in the magnitude of the interaction energy from that predicted theoretically. We attribute this effect to interference of bulk electronic states with the surface state [18,31]. Second, for a quantitative comparison with theory, we used the same model, shown as Eq. (2), by Hyldgaard and Persson [30], which fit the experimental data well over a selected distance range of 10–80 Å (solid line, inset of Fig. 3).

$$E(r) = -A(\delta_F, r) \left(\frac{4\varepsilon_F}{\pi^2} \right) \frac{\sin(2q_F d + 2\delta_F)}{(q_F d)^2}, \quad (2)$$

where δ_F is the phase shift, ε_F is the Fermi energy, q_F is the Fermi level wave vector, d is the distance, and A is a dimensionless value representing the interaction strength. The fit (dashed line, inset of Fig. 3) is based on Eq. (2) with $A = 480$ and $\delta_F = \pi/2$. The measured phase shift is in good agreement with previous values [19]. Our value of A for the interaction strength between two Br adatom islands is $\sim 10^2$ higher than for single metal adatoms. We attribute this difference to the multiple scattering sites along the edges of the islands and the highly electronegative Br being a strong scatterer [32].

The role of the surface state is prominent throughout this study. Experimentally measured separations reveal a relatively higher degree of spread; we attribute this to two main factors: thermal effects, since the islands were formed at ~ 600 K [21] and variety in the island shapes.

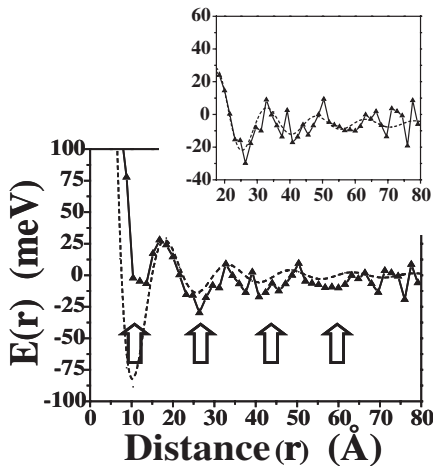


FIG. 3. Interisland interaction potential determined from the data shown in Fig. 2(d). The experimentally derived potential energy (solid line) is overlaid with a theoretically derived plot (dashed line) illustrating the oscillations at 15 Å intervals as well as the decay of the interaction energy as $1/r^2$ with distance r . Arrows indicate the four potential energy minima at 12, 26, 41, and 56 Å. Inset: Experiment (solid line) with theoretical fit (dashed line) based on Eq. (2) with $A = 480$ and $\delta_F = \pi/2$.

In order to determine the exact locations of the scattering centers, we performed alternate analyses by measuring island-island separations from the centers of each island, but did *not* observe similar oscillations in the corresponding interaction potential plot [33]. Therefore, the edges of the islands are the strong scattering sites and hence mediate the distribution of the islands. This is apparent in Figs. 2(a) and 2(b), where the surface-state electrons scattered from Br adatom islands on the terrace and at the top of the step follow the shapes of the island edges. In our experiment, the isolated, random distribution of the Br adatoms represents the locations at which the C_6H_5Br dissociatively chemisorbed on the Cu surface [22,24]. The 2D Br adatom islands were formed as a result of thermal diffusion of the isolated adatoms during the annealing step up to 600 K. We estimate a 112 meV barrier to diffusion for atomic Br, based on the experimentally measured value for atomic Cl on Cu(111) and the ratio of bond dissociation energies of Cu-Cl/Cu-Br [34–36]. In our experiments, the Br adatoms within each island were ordered, but the shapes of the islands depend on the edges [Figs. 2(a) and 2(b)]. We hypothesize that during the annealing step, the Br adatoms become mobile and aggregate into ordered nucleating sites due to favorable short-range interactions between the Br adatoms; however, their shapes and their lateral distribution were also influenced by the perturbed surface state of Cu(111). The edges of the islands form last [37–40]; adatoms diffuse along the contours of the ordered Br island nuclei while “communicating” with the neighboring islands via the surface-state electrons, thereby determining the most favorable interisland distances. Hence, calculating the relevant barrier to diffusion in our experiment is not trivial.

The coherence length of standing wave patterns is inversely proportional to the temperature of the surface, especially at $T > 100$ K where Fermi-Dirac broadening is the predominant factor in the damping process [41,42]. This coherence length (λ_c) as a function of temperature (T) for surface-state electrons on a bare noble metal surface can be calculated from the following equation [41]:

$$\lambda_c \cong \frac{\hbar^2 k_F}{3.5 m^* k_B T}, \quad (3)$$

where k_F is the Fermi level wave vector of the surface state, and m^* is the effective mass of a surface-state electron. The temperature dependence of the coherence length of the standing waves has been determined by Fujita *et al.* using STM [41]. In our experiment, the coherence length of standing waves at 600 K on bare Cu(111) (the temperature at which the Br islands were formed) is expected to be ca. 22 Å based on Eq. (3). We measured a decay length of ca. 19 ± 3 Å for the island-island interaction potential [43], while the oscillations were observed up to a distance of ca. 56 Å. The decay length of the interaction potential, 19 ± 3 Å, is in good agreement with the theoretically expected coherence length (ca. 22 Å) for standing waves at ~ 600 K on Cu(111), indicating the role of the surface state in the interisland distance distribution at 600 K. Although

the interisland distances reflect a coherence length of ca. 22 Å for standing waves at 600 K, STM images acquired at 4 K [Fig. 2(c)] indicate much longer coherence lengths, in agreement with previous observations.

Previous experiments showed that at low temperatures, going from adatom-adatom interactions [Co, Cu/Cu(111) at 9–12 K] to adatom-dimer interactions [Cu/Ag(111) at 6–25 K] [19,44], the distance over which oscillations in the interaction potential were observed increased from 80 to 230 Å. The increase in the attractive and repulsive strengths of the interaction potential for this adatom-dimer experiment was estimated to be ± 1 meV [44]. In our experiments, the energy barrier from the first minimum at 12 Å to the first maximum at 18 Å is ~ 25 meV, substantially higher [18,19,44]. The origins of this striking difference between the energy barriers are twofold: there are multiple Br adatoms at the edges of the islands, and the Br adatoms themselves are stronger scatterers. We postulate that, due to anisotropy of the Br-Cu bond, Br adatoms present a larger barrier to the surface-state electrons than do Cu adatoms; thus, Br is a stronger scatterer than Cu, and we measure a stronger island-island interaction potential.

We have extended the understanding of the role of the surface state in mediating interactions between single adsorbates at low temperatures to that of larger aggregates of adsorbates at catalytically relevant temperatures. Our analyses show oscillations in the interisland interaction potential with a periodicity of $(\lambda_F/2)$ of Cu(111) up to a distance ca. 56 Å. The attractive and repulsive strengths of the interaction potential are attributed to the strong perturbation of the surface state by the Br adatom islands. By selecting an adsorbate that interacts strongly with the substrate, we have demonstrated the vital role of the substrate surface state in mediating interactions between adsorbates, even at elevated temperatures.

We thank Professor K. Fichthorn, Dr. A. Soudackov, and Dr. S.-C. Li for insightful discussions. We also gratefully acknowledge the financial support of NSF and ONR.

*Corresponding author.

Email address: stm@psu.edu

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