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How Atomic Steps Modify Diffusion and Inter-adsorbate Forces: Empirical Evidence from Hopping Dynamics in Na/Cu(115)

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Ⓢ *Supporting Information*

ABSTRACT: We followed the collective atomic-scale motion of Na atoms on a vicinal Cu(115) surface within a time scale of pico- to nanoseconds using helium spin echo spectroscopy. The well-defined stepped structure of Cu(115) allows us to study the effect that atomic steps have on the adsorption properties, the rate for motion parallel and perpendicular to the step edge, and the interaction between the Na atoms. With the support of a molecular dynamics simulation we show that the Na atoms perform strongly anisotropic 1D hopping motion parallel to the step edges. Furthermore, we observe that the spatial and temporal correlations between the Na atoms that lead to collective motion are also anisotropic, suggesting the steps efficiently screen the lateral interaction between Na atoms residing on different terraces.
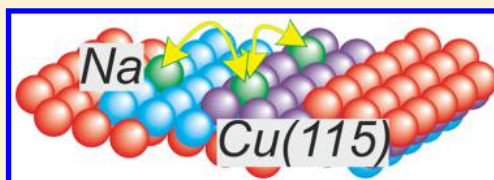
Single atomic steps are the dominant surface defect, even on a carefully prepared surface. It is widely accepted that atomic steps play an important role in surface diffusion of add-atoms and adsorbates, and hence their existence and density is expected to modify the growth mode of thin layers, heterogeneous catalysis, and many other surface systems, which are limited by the diffusion rate. Furthermore, it has been hypothesized that atomic steps are responsible for controversies and discrepancies between diffusion measurements performed with techniques that have different spatial resolutions.[1,2]

Significant efforts have been made to measure the effect steps have on surface diffusion of adsorbates over the years. Macroscopic techniques that measure variations in coverage on a micron scale have shown the cumulative effect of a large number of atomic steps, clearly demonstrating the anisotropic nature of the motion and the changes in the activation energies for diffusion.[3,4] Unfortunately, experimental data for the atomic-scale motion of an adsorbate near a step edge are particularly scarce. The tendency of adsorbates to be trapped at step sites makes it difficult, if not impossible, to study the diffusion near a step using low-temperature scanning tunneling microscopy due to its limited dynamical range. Under certain conditions, adsorbates can be released from the steps using energetic photons in pump–probe experiments, providing valuable insight into the dynamics of the excited adsorbate.[5,6] In contrast, when it comes to studying how the steps modify the individual and collective atomic-scale motion of adsorbates in thermal equilibrium, the experimental database is essentially nonexistent, leaving us with an understanding based solely on theoretical approaches.[2,7]

In this work, we present measurements of the atomic-scale motion of Na atoms on a Cu(115) surface. The well-defined geometry of a densely stepped vicinal surface such as Cu(115)[8] provides a controlled environment for studying the role atomic steps have on diffusion. Because the motion of Na on Cu(100) surface has been thoroughly studied in the last two decades,[9−12] working with the Cu(115) surface provides an excellent opportunity to focus on the changes induced by the presence of atomic steps. The transition from the relatively flat Cu(100) surface to a stepped surface raises several questions and unknowns, in particular: which are the available adsorption sites on this surface and to what extent do the atomic steps modify the diffusion, both parallel and perpendicular to the step direction? Another question, which is typically inaccessible to experiments, is whether the steps affect the lateral interactions between the adsorbed atoms, that is, the collective diffusion process. We combine experimental data with molecular dynamics (MD) simulations to address these questions and show that atomic steps radically change the nature of the atomic-scale diffusion.

The Cu(115) sample studied in this work is a vicinal surface with (100) terraces and a very small step separation of 6.63 Å. The schematic drawing in Figure 1 illustrates the geometry of the surface viewed from above and from the side. The clean Cu(115) surface has been shown to be a stable vicinal surface below the roughening transition (380 K).[13] Adsorption of alkali metals at high coverages and temperatures can initiate a surface
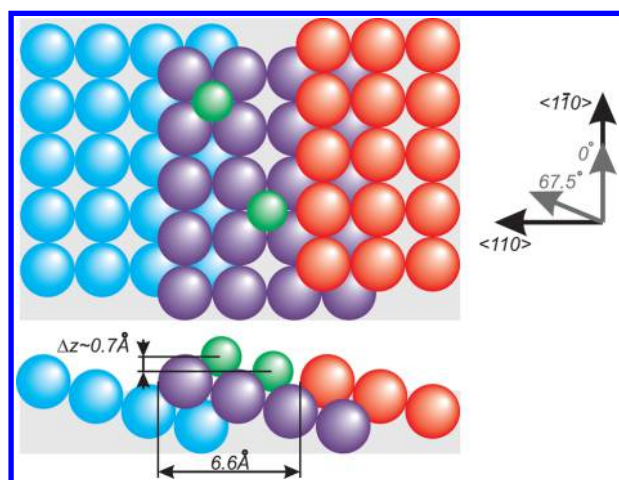
Figure 1. Schematic drawing of the Cu(115) surface viewed from above and from the side and a definition for the 0 and 67.5° azimuths referred to in the text. The copper atoms of the different layers are drawn with different colored spheres; smaller green spheres illustrate a hypothetical scenario of Na atom moving in between hollow cites, emphasizing that such a motion would also have a component perpendicular to the surface.

reconstruction.[14] In this study, we have limited ourselves to relatively low coverages and temperatures where the surface does not undergo any major reconstruction, verified using helium diffraction before and after Na adsorption.

The experimental technique used in this study is helium spin echo (HeSE) spectroscopy. In a HeSE experiment the nuclear spin of ^{3}He is manipulated using magnetic fields resulting in an atom interferometer setup, capable of measuring atomic-scale motion in reciprocal space on a unique time range of pico- to nanoseconds. In the text below, we provide a brief description of the quantities measured by this technique; a detailed explanation can be found elsewhere.[15,16]

Within the kinematic scattering approximation, the HeSE apparatus measures the intermediate scattering function, ISF, $I(\Delta\vec{k}, t) \propto \langle \sum_i \sum_j e^{-i\Delta\vec{k}\cdot\vec{R}_i(0)} e^{-i\Delta\vec{k}\cdot\vec{R}_j(t)} \rangle$. $\Delta\vec{k}$ is the momentum exchanged during the scattering of the helium atom (divided by $\hbar$) consisting of a component parallel to the surface, $\Delta\vec{K}$, and a component perpendicular to the surface, Δk_z. $\vec{R}_i(0)$ and $\vec{R}_j(t)$ are the position vectors of surface atoms (scattering centers) i and j at times 0 and t, respectively, the double sum is over all possible pairs of surface atoms and the brackets denote an ensemble average.[2] When the coverages are low and the interaction between the adsorbed species is negligible, the ISF is dominated by the $i = j$ terms (self-correlation). In this case, the diffusion of an adsorbed atom, i, increases the difference between $\vec{R}_i(0)$ and $\vec{R}_i(t)$, resulting in a random phase of the complex exponent (loss of spatial and temporal self-correlation) and a decay of the ISF to zero with increasing time. When the interaction between the adsorbed atoms is non-negligible, the ISF decay reflects the loss of self-correlation as well as the loss of correlation between pairs of adsorbates due to the dynamics. Hence, measuring correlation functions such as the ISF does not restrict the data
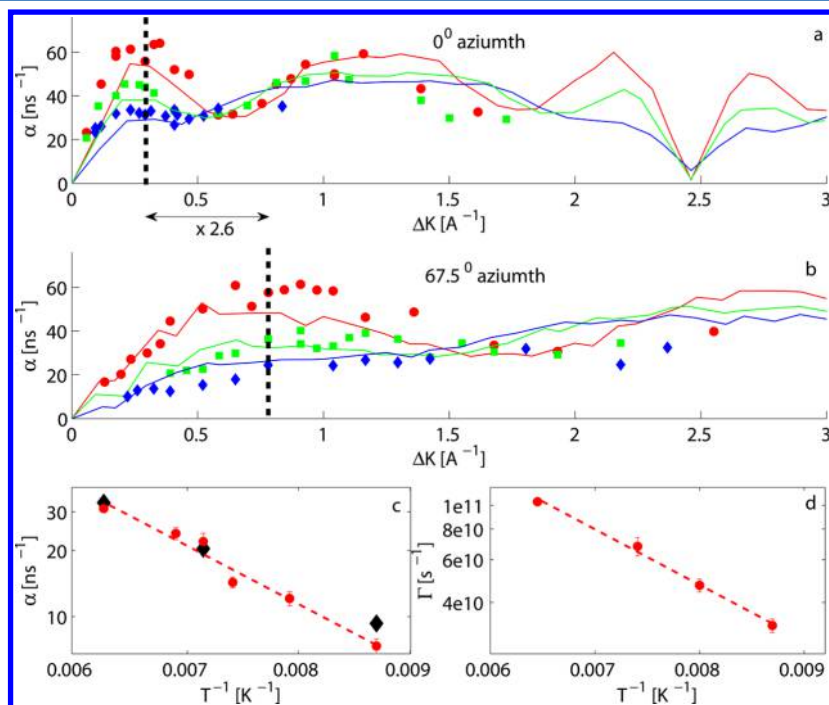
Figure 2. Full symbols show the extracted decay rates, α, of the measured ISF as a function of ΔK, measured along the 0° azimuth (a) and along the 67.5° azimuth (b). Red circles, green squares, and blue diamond symbols mark Na coverages of 0.095, 0.075, and 0.05 ML, respectively. All measurements were performed at 155 K. The dashed vertical lines mark the approximate position of the correlation peak, which is scaled by a factor of 2.6 when moving from the 0 to the 67.5° azimuth. The full lines show the MD simulation results when using a high step-crossing barrier and an anisotropic Na−Na interaction for the different coverages. (c) Temperature dependence of α, measured along the 0° azimuth, $\Delta K = 0.65$ Å^{-1} at a Na coverage of 0.09 ML. Red circular markers are the experimental values, the dashed red line is an Arrhenius fit with an activation energy of 53 ± 5 meV, and the black diamond markers are results of the MD simulation using the best-fit parameters described in the text. (d) Temperature-dependent Na hopping rates extracted from the simulated trajectories.
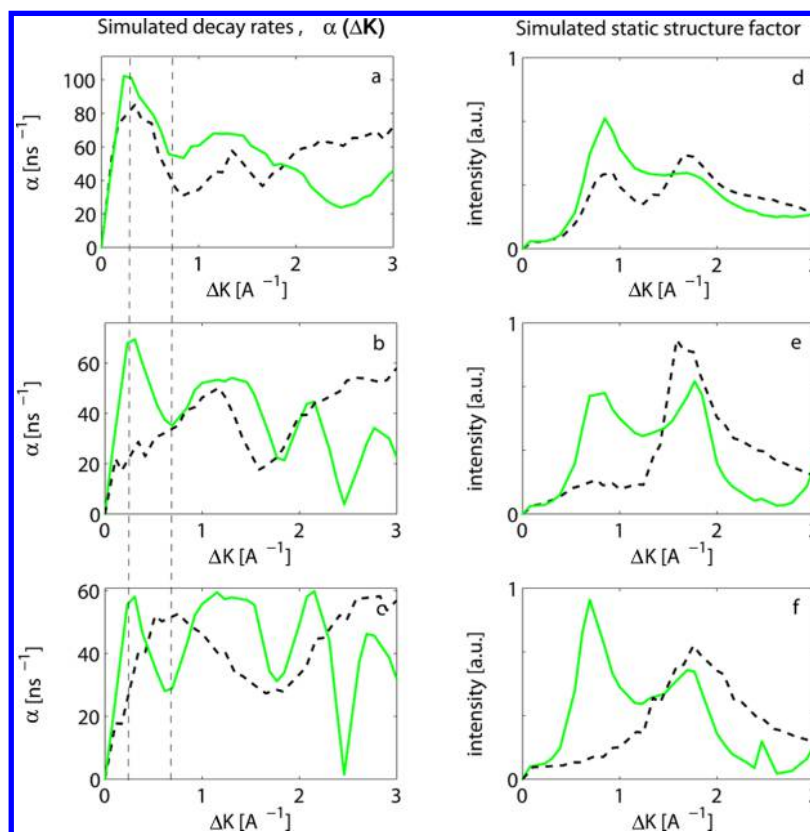
Figure 3. MD simulations of $\alpha(\Delta K)$ curves (left panels) and static structure factors (right panels) for a Na coverage of 0.095 ML, T = 155 K, along the 0 (solid green line) and 67.5° (dashed black line) azimuths, respectively. Panels a and d show results for a negligible (10 meV) step-crossing barrier, panels b and e are for a high step-crossing barrier (70 meV higher than the energy barrier for diffusion along the step edges), and panels c and f are for the same (70 meV) step-crossing barrier when using an anisotropic interaction model, which screens the interaction between Na atoms on different terraces.

interpretation to a single parameter such as the tracer (self) or chemical (collective) diffusion coefficients; rather, it supplies a full picture that allows us to study both of these processes.[2] In many cases, including this work, the time dependence of the ISF is well approximated by a simple exponential decay, $I(\Delta \vec{k}, t) = Ae^{-\alpha t}$, such that the $\Delta \vec{k}$, temperature, and adsorbate coverage dependencies of the decay rates, α, supply a detailed picture of the microscopic diffusion process, the energy barriers for diffusion, the frictional coupling to the surface, and a unique opportunity to measure interadsorbate forces.[12,16,17]

To study the directionality of the surface diffusion, we measured the ISF along two different crystal azimuths. A natural choice would be to measure parallel and perpendicular to the step edges, along the $<1\bar{1}0>$ and $<110>$ crystal azimuths. On the flat surface these azimuths should give identical results, and any differences between the two could be used to quantify the effects steps have on the motion; however, along the $<110>$ direction the signal is overwhelmed by elastic scattering from the Bragg peaks of the stepped structure and hence we chose a second azimuth that is 67.5° from $<1\bar{1}0>$, which is sufficiently far from the Bragg peaks yet still provides insight into the anisotropic nature of the surface. The two azimuths are illustrated in Figure 1 and are referred to in the text as the 0 and 67.5° azimuths. The full symbols in Figure 2a show the extracted decay rates, α, of the measured ISF as a function of ΔK, measured along the 0° crystal azimuth. The measurements were performed at 155 K for Na coverages of 0.05, 0.075, and 0.095 ML. (1 ML is defined as 1 Na atom per surface area of 2.55 Å × 2.55 Å for easier comparison with the Cu(100)

surface.) A few observations can be readily made from the measured decay rates. (I) The decay rate at low ΔK values increases significantly with coverage producing a peak followed by a dip: We will denote these features the correlation peak and the de Gennes narrowing dip. (The de Gennes narrowing is termed by analogy to the features seen in neutron scattering from correlated liquids,[18] simply speaking the idea is that the repulsive forces lead to preferred length scales where the system is stable and correspondingly the energy width (or decay rate) is at a minimum at the corresponding wave vector values. A more detailed explanation of the phenomena is given in a review of the HeSE technique.[16]) The de Gennes narrowing dip is located at ~0.65 Å^{-1} for the highest coverage and both shifts to lower ΔK values and becomes less pronounced as the coverage is decreased. A similar coverage dependency was seen on Na/Cu(100) and is characteristic of correlated motion, driven by long-range repulsive dipole–dipole interaction between the Na atoms. (Alkali atoms, like many other atomic and molecular adsorbates, transfer charge to the underlying metallic substrate resulting in significant dipole moments.[19]) (II) A second maximum can be seen at ~1.2 Å^{-1}, a peak that was also seen for Na/Cu(100). This peak matches the expected maximum position of α in the Chudley Elliot model[20] if the Na atoms are jumping between adjacent adsorption sites, which follow the copper atoms spacing of 2.55 Å. This observation is consistent with the fact that the terraces on the Cu(115) have a (100) geometry. (III) For all three coverages the decay rates seem to reduce toward zero as ΔK approaches zero. At this limit, the only momentum exchanged upon scattering is

perpendicular to the surface. Correspondingly, the scalar product in the ISF involves only motion perpendicular to the surface. Thus, a vanishing $\alpha(\Delta K \rightarrow 0)$ means that the motion we measure is predominantly within the surface plane.

Observations (I) and (II) tell us that Na atoms perform jump diffusion with a typical jump distance equal to the lattice spacing and that the Na atoms significantly repel each other. Observation (III) shows us that the complex 3D motion, which was seen at high coverages (>0.05 ML) for Na/Cu(100),[12] plays a negligible role on this surface, within the coverage range we measured. Furthermore, the third observation also provides insight regarding the number of adsorption sites within the width of a single terrace. In particular, one could naively hypothesize that the Na atoms occupy the hollow sites on both sides of the terrace (green spheres in Figure 1) and jump between these sites, similarly to the motion of Na on a flat Cu(100) surface. Because of the skewed nature of this surface, this type of motion should change both the lateral position and the height of the atoms, leading to a nonvanishing $\alpha(\Delta K \rightarrow 0)$, in contrast with our experimental observations. It is important to note that the helium atoms scatter from the electron density[21] and hence observation (III) on its own does not completely rule out motion between adsorption sites on both sides of the terrace if for some reason the electron density of this surface deviates substantially from the geometrical model shown schematically in Figure 1.

Further insight is obtained from measurements along the 67.5° azimuth. The full symbols in Figure 2b are the extracted decay rates, $\alpha(\Delta K)$, measured along the 67.5° azimuth at 155 K for the same three coverages plotted in Figure 2a. It is immediately obvious that the ΔK dependence is very different to that measured along the 0° azimuth; that is, the diffusive motion is clearly anisotropic. In fact, the curves in Figure 2b approximately overlap those shown in Figure 2a if one scales the two horizontal axes using a factor of 2.6, illustrated by the dashed vertical lines in Figure 2a,b, which mark the approximate position of the correlation peak for each of the two azimuths. A simple stretching of the ΔK axis between the two measurements suggests 1d motion, which is purely parallel to the atomic steps. This can be understood from the fact that the dephasing of the ISF is given by the scalar product $\Delta \vec{k} \cdot \vec{R}$. Consequently, the projection of a 1d jump between adjacent adsorption sites onto the 67.5° direction is $\cos(67.5) = 1/2.6$ shorter, stretching the ΔK dependency by the reciprocal factor.

The simple scaling relation between the $\alpha(\Delta K)$ curves of the two azimuths excludes significant motion perpendicular to the step edges that would produce additional Chudley–Elliot oscillations and a completely different $\alpha(\Delta K)$ shape.[20] This finding strengthens our previous conclusion that the Na atoms are not jumping in between two different sites within the width of the terrace, regardless of whether the surface corrugation probed by the helium atoms follows the schematic shown in Figure 1. Moreover, the energy barrier for jumping between different terraces must be considerably higher than that for motion in the parallel direction, resulting in a negligible contribution to the decay rates, α, from jumping in between adjacent terraces.

To complement these qualitative arguments, we performed a quantitative MD simulation analysis. These Langevin-based simulations have been used successfully for studying isolated and correlated diffusion.[12,16] Details of the simulation are given in the Supporting Information (SI). Figure 3a shows calculated $\alpha(\Delta K)$ curves for the two azimuths using a negligible energy barrier for step crossing. The full green lines and dashed black lines mark the 0 and 67.5° azimuths, respectively. As expected, the relatively isotropic motion leads to similar $\alpha(\Delta K)$ curves for the two azimuths, which are very different to the experimental results. Figure 3b shows calculations with a high energy barrier, which effectively blocks step crossing completely. The anisotropic motion leads to a clear difference between the two azimuths, supporting our qualitative arguments; however, the initial correlation peak followed by the de Gennes narrowing dip, related to the relative motion of Na atoms, does not follow the same simple scaling behavior seen in the experimental data. Instead, along the 67.5 azimuth we see a broad peak with a maximum at ~1.2 Å^{-1}. (The vertical dashed lines mark the positions of the two peaks in the experimental data, shown also in Figures 2a,b.)

An explanation for this discrepancy can be seen when comparing the static structure factor (SSF), $I(\Delta \vec{k}, t = 0)$. The SSF, which is simply the Fourier transform of the average pair distribution function and effectively gives the same information as a diffraction pattern, is plotted on the right panels of Figure 3. For a negligible step-crossing barrier, the SSF (Figure 3d), has a well-defined peak at ~0.8 Å^{-1}, reflecting a typical Na spacing of $2\pi/0.8 = 8$ Å. This peak appears roughly at the same position along the two azimuths due to the almost isotropic motion obtained in the absence of a significant step-crossing barrier. (A peak in the static structure factor gives rise to a de Gennes narrowing dip in $\alpha(\Delta K)$ at roughly the same position; this relation can be derived from analytical theory[2] and is also obvious when comparing Figure 3a,d.) Figure 3e shows the SSF in the presence of a significant step-crossing barrier. While there is a significant difference between the two azimuths, the 67.5° azimuth still contains a peak in the SSF at ~0.8 Å^{-1}, even though its intensity is smaller. The fact that our simulation calculates a structure peak at approximately the same position along both azimuths reflects the fact that we have used an isotropic Na–Na interaction model that maintains the typical distances and correlated motion between Na atoms on different terraces.

Figure 3c,f shows $\alpha(\Delta K)$ and the SSF when using a modified simulation which includes a screening effect of the atomic steps; that is, the repulsive force was set to zero between Na atoms on different terraces. As can be seen, making the interaction anisotropic removes the static structure factor peak at ~0.8 Å^{-1} and results in a $\alpha(\Delta K)$ curve for the 67.5° azimuth, which looks like a simple stretch of the 0° azimuth, now consistent with the trend in the experimental data.

A quantitative description of the diffusion process was obtained by simultaneously fitting the measured ΔK, crystal azimuth, coverage, and temperature dependencies (Figure 2a–c) of the decay rates, α. The potential energy surface we used contains only one adsorption site within the width of the terrace and has two adjustable parameters, an energy barrier for moving along the steps, E_{bridge}, and a barrier for step-crossing E_{step}. A repulsive dipolar interaction model was used[12] with the important modification that interactions were only allowed between Na atoms on the same terrace, that is, an anisotropic interaction. The lines in Figure 2a,b show the simulated results for the best-fit parameters, $E_{bridge} = 55$ meV and $E_{step} \geq 125$ meV. (Higher values did not make a noticeable difference.) The simulated α values reproduce all of the major trends previously discussed, and given the relatively simple model used and the minimal number of adjustable parameters the simulation mimics the data surprisingly well. Given the good fit between

the experiments and the MD simulation, we can use the latter to calculate the hopping frequency of the Na atoms. These hopping rates, which are plotted in Figure 2d, follow a simple Arrhenius behavior with an activation energy of 43 ± 3 meV and a pre-exponential factor of $2.7 \pm 0.6 \times 10^{12}$ s^{-1}. It is interesting to note that these hopping rates, which are predominantly in the 0° azimuth, are significantly faster ($\approx \times 4$ at 155 K) than on Na/Cu(001) at similar temperatures, reflecting the fact the barrier is lowered by 20 meV, resembling the macroscopic observations of CO on platinum surfaces.[3]

In summary, from the lack of motion perpendicular to the surface plane and the comparison between the measured ISF along the two azimuths, we conclude that the motion of the Na atoms involves only one adsorption site per terrace and that the motion is strongly oriented parallel to the step edges. (It is important to note that we can not identify the exact position of the single adsorption site from which the diffusion takes place, that is, whether it is located in the middle of the terrace or close to the upper or lower step, based on the diffusion data. Consequently, the choice of a PES with a minimum at the center of the terrace, as shown in the SI, is based on simplicity and convenience.) This observation could indicate either that there is only one minimum of the PES within the terrace width or that Na atoms also reside in other adsorption sites, which have significantly larger energy barriers (>120 meV) for diffusion and hence do not contribute to the measured dynamics. Future helium or electron diffraction studies as well as measurements of the vibrational frequencies of Na/Cu(115) could potentially differentiate between these two scenarios. Comparison with MD simulations reveals that not only do the atomic steps dramatically limit the diffusion across the steps (by at least 2 orders of magnitude at 155 K) and increase the rate of motion along the steps but they also effectively shield the Na–Na interaction, making the spatial and temporal correlations between Na atoms highly anisotropic as well.

Atomic steps on bare metallic surfaces produce significant permanent dipoles.[22] It seems plausible that Na atoms produce induced dipoles at the step edges that oppose the repulsive force between Na atoms on different terraces and lead to a loss of temporal and spatial correlation. Because atomic steps are such a common surface defect and many atomic and molecular adsorbates experience dipolar interactions, our observation of how steps affect adsorbate diffusion is likely to be relevant to a wide range of surface systems. In particular, the screening effect of the atomic steps that makes the correlated motion anisotropic should be considered when designing vicinal surface templates for self-organized nanostructures (e.g., ref 23). Finally, Alkali atoms on copper surfaces also represent a rather unique case where DFT calculations coincide with diffusion data to a very high accuracy.[24] Hence, the atomic-scale diffusion measurements presented above provide a benchmark for testing how well DFT can explain and eventually predict the effect steps have on diffusion and on the interaction between adsorbates on surfaces.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.5b01939.

> Description of the experimental methods. Angular scans along the 90° azimuth. An example of a measured ISF

curve from which the decay rates are extracted. Description of the molecular dynamics simulation. MD simulations of a PES with two adsorption sites within the terrace width. (PDF)

Movie illustrating the correlation of the trajectories under the nonisotropic interaction potential. (AVI)

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Notes
The authors declare no competing financial interest.

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