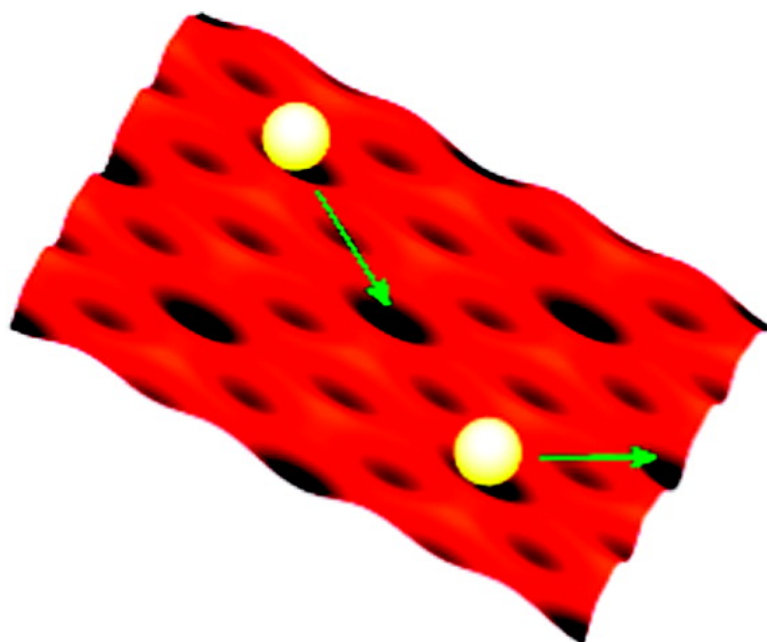


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Observation of Uncorrelated Microscopic Motion in a Strongly Interacting Adsorbate System

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Abstract: Modeling of intermolecular forces is a central theme in the physical sciences. The prototypical heterogeneous catalysis system, CO/Pt(111), is an extensively studied example where strong pairwise repulsive forces between the CO molecules have been used to explain the observed structure and dynamics. No direct measurements of these forces were available; yet, they offered a natural way of explaining various macroscopic observations assuming a separable adsorbate–substrate interaction and pairwise adsorbate–adsorbate interactions. In the present study, we measure intermolecular forces by following CO motion on a microscopic scale. The uncorrelated dynamics we observe throughout the coverage range of the measurements excludes the existence of the strong pairwise forces previously suggested. The increase in the rate of uncorrelated motion is explained by a nonlocal modification of the adsorbate–substrate interaction, reflecting a many-body system that cannot be described by the standard separable interaction approach.

Introduction

Atomic-scale forces between adsorbates on a surface play a crucial role in a wide range of phenomena, ranging from chemical reaction, epitaxial growth, and phase transitions to the growing field of nanoscale technology. The magnitudes of these forces are frequently deduced indirectly from macroscopic measurements by using simplifying approximations for the nature of the interaction. The chemisorption of CO on the Pt(111) surface is considered by many as the prototypical heterogeneous catalysis system. It has been studied for decades and is still a topic of ongoing theoretical and experimental research.^{1,2} Both the heat of adsorption and the desorption temperature drop as the CO coverage increases.^{3–5} These changes have been interpreted as an indication of strong pairwise repulsive forces between the CO molecules.^{3,6,7}

Although these pairwise forces have not previously been measured directly, their deduction from energetic data is a well-established surface science practice and follows an assumption

which we shall refer to as the separable pairwise interaction (SPI) approximation. Within the SPI approximation, the energetics of the system are separated into two terms: the first represents the interaction between an isolated adsorbate and the substrate, also known as the potential energy surface (PES), and the second is a sum over all the pairwise adsorbate–adsorbate interactions which could be either direct electrostatic interactions or more complex substrate-mediated interactions,⁸ whatever their origin.

The SPI approximation enables the determination of inter-adsorbate forces from macroscopic adsorption properties and facilitates numerical modeling of systems with many particles.⁹ Although these advantages have made the SPI approximation very popular with surface scientists, the validity of reducing the many-body problem of an adsorbate system to the two separable terms is not necessarily guaranteed. Pairwise forces, regardless of their origin, that is, whether direct or substrate-mediated, necessarily generate collective motion of the adsorbed species. By using a ³He spin-echo (³HeSE) spectrometer,¹⁰ we have measured the collective motion of CO molecules in thermal equilibrium on a Pt(111) surface and studied the underlying atomic scale interactions. Our observations highlight the problematic nature of the standard interpretation of adsorption properties and supply experimental evidence for a system characterized by intermolecular interactions that are of a complex many-body nature, well beyond the validity of the SPI model.

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Experimental Technique

The $^3\text{HeSE}$ experiment is a surface analogue of the well-established neutron spin-echo experiment.¹¹ In the $^3\text{HeSE}$ experiment, a thermal energy ^3He beam is scattered from the sample, providing a surface-sensitive probe for measuring ultrafast dynamics in equilibrium. The unique temporal sensitivity of this technique, coupled with the atomic-scale wavelength of the ^3He beam, enables measurements on a time and length scale previously inaccessible to experiment.^{12,13} An explanation of the technique and a review of some recent results can be found elsewhere.¹⁴

Within the kinematic single-scattering approximation, the observable quantity in a $^3\text{HeSE}$ experiment is proportional to the intermediate scattering function (ISF), $I(\Delta K, t)$. [Previous numerical work¹⁵ demonstrates that including multiple scattering contributions does not alter the width of the quasielastic peak and hence the time dependence of the spin-echo measurement.] The ISF, also referred to as the time-dependent dynamic structure factor,¹⁶ is the spatial Fourier transform of the pair correlation function, $G(R, t)$, which describes the probability of finding a particle at position R and time t , given the existence of a particle at $R = 0$, $t = 0$.^{17,18} Thus, the $^3\text{HeSE}$ experiment measures the complete nature of the surface motion and not just the mobility rate or the diffusion energy barrier. The reciprocal space variable, ΔK , is referred to as the momentum transfer and is given by the momentum transfer of the scattering event within the surface plane, $\Delta K = \Delta P/\hbar$. In the present study, the momentum transfer is varied by changing the scattering angle of the beam. [Following the usual convention, capital letters denote 2D vectors within the surface plane.] The time interval, t , within which the motion on the sample is measured, is also known as the spin-echo time.¹¹ In the Cambridge apparatus,¹⁹ t can be scanned within the subpicosecond–nanosecond range.

Generally speaking, when random motion takes place on a surface, the ISF decays with time. The rate of this decay is governed by the lifetime of the transient surface structures which scatter the ^3He beam. In order to study the microscopic mechanism that underlies the dynamics, the functional form and the rate of this decay are measured for different experimental conditions.¹⁴ For simple diffusion mechanisms such as continuous random motion or discrete jump diffusion, the temporal decay is exponential, that is, $I(\Delta K, t) \propto \exp\{-\alpha(\Delta K)t\}$. When this is the case, the momentum-transfer dependence of the inverse lifetime, $\alpha(\Delta K)$, and the way α changes with sample temperature and adsorbate coverage can be used to study the adsorbate dynamics and the interactions that govern the dynamics.^{12,13} Indeed, in the present study, the ISF exhibits a simple exponential decay with time. Thus, the inverse lifetime, α , extracted from an exponential fit to the data, will be used below to characterize the ISF and the corresponding surface dynamics.

Results and Analysis

The markers in Figure 1 show the inverse lifetime values, α , at a surface temperature of 340 K for different surface coverages. The inverse lifetimes increase with momentum transfer, reaching a maximum at $\sim 1.3 \text{ \AA}^{-1}$, as expected for jump diffusion, when the dominant jump length is between adjacent top sites.²⁰ The

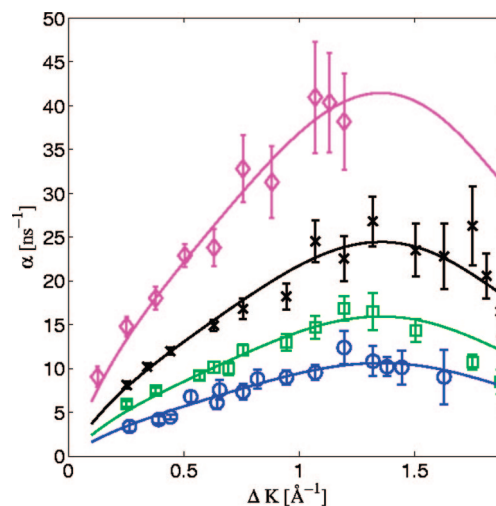


Figure 1. Inverse lifetime as a function of the momentum transfer, $\alpha(\Delta K)$, measured for CO/Pt(111) at 340 K along the $\langle 11\bar{2} \rangle$ crystal azimuth. The circle, square, cross, and diamond markers were measured for coverages of $\Theta = 0.065, 0.165, 0.22,$ and 0.3 ML , respectively. The solid lines show the same polynomial function scaled by a factor of 1.0, 1.5, 2.3, and 3.9 for the four different coverages. The fact that a simple scaling factor is sufficient to fit the coverage dependency within the accuracy of the data illustrates the constant shape of $\alpha(\Delta K)$ and the lack of correlation in the motion of the CO molecules.

absolute values of α are strongly coverage-dependent and indicate that the hopping rate increases with coverage. However, within the experimental accuracy, the functional form of $\alpha(\Delta K)$ does not change shape as the coverage increases. The constancy of the $\alpha(\Delta K)$ shape is illustrated by the continuous curves in Figure 1, which all have the same functional form, differing only by a scaling factor.

The fact that $I(\Delta K, t)$ and correspondingly the pair correlation function are coverage-dependent reflects a coverage dependence of the microscopic diffusion properties, which is consistent with previous macroscopic diffusion studies.²¹ However, the fact that the $\alpha(\Delta K)$ curve maintains its shape with increasing coverage is both surprising and important. As we show below, a shape that is coverage-independent tells us immediately that the pairwise repulsive forces between CO molecules are practically negligible and, contrary to previous suggestions,²¹ are not responsible for the significant increase in the CO mobility with increasing coverage.

The relation between pairwise forces and the inverse lifetimes, α , has been the subject of existing analytical, numerical, and experimental studies.^{15,22–24} When significant pairwise forces exist between the adsorbates, they lead to temporal and spatial correlation between the adsorbates, resulting in surface dynamics and a corresponding ISF that change as a function of coverage. In particular, when correlations are accounted for, the way in which pairwise forces alter the motion does not change the inverse lifetimes, α , uniformly for different (ΔK) values. Instead, the pairwise forces will lead to a modulation pattern, which

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changes the form of $\alpha(\Delta K)$ as a function of the adsorbate coverage. This modulation in the form of $\alpha(\Delta K)$ is a 2D analogue of the well-known DeGennes narrowing seen in neutron scattering experiments,²⁵ and its origin is explained qualitatively in the first section of the Supporting Information. In the text below, we present a numerical analysis that demonstrates the inability of pairwise forces to reproduce the observed, coverage-dependent dynamics both quantitatively and qualitatively.

We start with molecular dynamics (MD) simulations within the SPI approximation.²⁶ These simulations include interactions explicitly and, therefore, go beyond approximate, stochastic treatments.²⁴ Trajectories of a particle of mass m_i , moving with a velocity of v_i , are traced within a 2D plane by using the Langevin equation.

$$m_i \ddot{u}_i = -\nabla U - \eta m_i \dot{u}_i + \sum_{j \neq i} F_{i,j} + \zeta(t) \quad (1)$$

Equation 1 includes three interactions that can be adjusted: the PES, U , which represents the interaction between an isolated CO molecule and the substrate, the friction coefficient, η , which represents the energy transfer rate between the CO molecules and the surface, and a pairwise force between the CO molecules, $F_{i,j}$. Random impulses, $\zeta(t)$, simulate the flow of energy from the surface to the molecules and are calculated from a gaussian distribution, the width of which is determined by η through fluctuation–dissipation theory.²⁷ For the present work we used a fixed value for the friction, $\eta = 0.7 \text{ ps}^{-1}$, derived from measurements of the total lifetime of the frustrated translational vibration.²⁸ By performing scattering calculations at each time step,²⁶ we obtain a numerical ISF from the trajectories, which we then compare with the experimental results.

The PES used in the simulations was constructed by using the first- and second-order Fourier components of the $\langle 111 \rangle$ unit cell, as described in more detail in the Supporting Information. Symmetry allows us to use only two parameters for both top-site and bridge-site adsorption. The position of the global minimum was assigned to the Pt top sites.²⁹ We chose the two free parameters to be the top–top diffusion barrier, U_{TT} , defined as the maximum value of U along the straight line which connects the two top sites, and $U_{\text{B}} - U_{\text{T}}$, which is the energy difference between the bridge and top sites. In order to optimize the PES in a way that is independent of the pairwise interaction, we fitted the PES parameters for the low-coverage measurement ($\Theta = 0.065 \text{ ML}$, Figure 1), obtaining $U_{\text{TT}}, U_{\text{B}} - U_{\text{T}} = 210$ and 95 meV . [The fact that we did not observe any further changes in the experimental results when the coverage was further reduced (data not shown) suggests that at this coverage, the effect of CO–CO interactions can be safely neglected.]

Next, we introduce a repulsive pairwise CO–CO interaction into the Langevin equation. We start with a repulsive interaction suggested by McEwen et al.⁷ In their recent comprehensive study, McEwen et al. made a novel attempt to explain simultaneously a large body of adsorption and desorption measurements performed on this system. In order to derive the strength of the CO–CO interaction from the various macroscopic measurements, McEwen et al. followed the standard

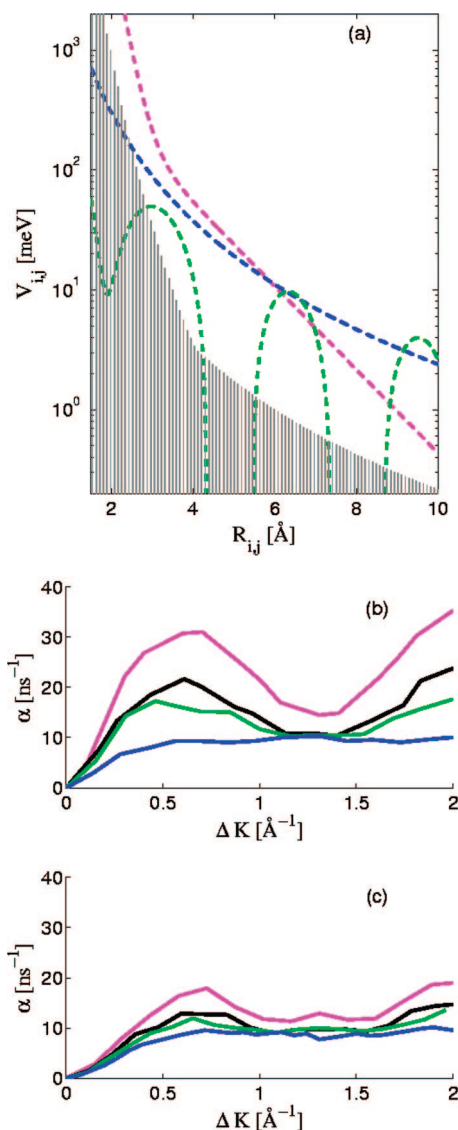


Figure 2. (a) Pairwise interactions considered in the text. The dashed blue line is the CR^{-3} , $C = 2.1 \times 10^3 \text{ meV } \text{Å}^3$, fit to the the McEwen interaction,⁷ whereas the dashed magenta line and the dashed green line are the interaction models used by Persson⁶ and Petrova et al.,³⁰ respectively. The shaded area marks the approximate region of possible interactions that do not result in significant correlation features, defined by the upper limits of a long-range (R^{-3}) and a short-range (R^{-8}) interactions. (b) Inverse lifetimes calculated from MD simulations which use the R^{-3} fit to the McEwen interaction, the different colors represent the same coverages as those plotted in Figure 1. (c) Calculated inverse lifetimes by using the nonmonotonic substrate mediated interaction derived by Petrova et al.

surface science practice and assumed the validity of the SPI approximation. The blue dashed line in Figure 2a shows a R^{-3} fit to these interactions (referred to as set2 in ref 7). Figure 2b shows the corresponding coverage dependency of the inverse lifetimes calculated from the MD simulations which included these CO–CO interactions. At the lowest coverage, where the effect of the forces is negligible, the simulated $\alpha(\Delta K)$ reproduces the experimental result. As the coverage increases, a significant change in the $\alpha(\Delta K)$ curve is observed, which corresponds to the enhanced lifetime of the preferred structure that we describe in the Supporting Information. The simulation is clearly not consistent with the fixed shape of the experimental data (Figure 1). It follows that any pairwise forces are much weaker than those predicted by McEwen et al. within the SPI assumption.

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The inability of pairwise interactions to produce a uniform increase in $\alpha(\Delta K)$ with increasing coverage is not unique to the McEwen interaction. It is a general effect as we now illustrate. Figure 2a shows two other pairwise interaction models which were derived to fit a particular CO/Pt(111) measurement: the substrate-mediated interaction suggested by Persson to explain Ertl's heat of adsorption measurements^{5,6} (dashed magenta line) and the substrate-mediated interaction suggested by Petrova et al. to explain the dynamics of the CO overstructures³⁰ (dashed green line). [Note that the vertical axis is presented with a logarithmic scale; hence, the negative values are omitted from the graph.] Simulating the Persson model, which is stronger at a short distance but has a shorter range compared with the McEwen interaction, results in a strong modulation pattern, very similar to the results obtained for the McEwen interaction (data not shown); that is, this force model also gives rise to an unrealistic CO–CO correlation. The oscillatory interaction suggested by Petrova et al. results in a weaker coverage dependency shown in Figure 2c. However, the smaller change in $\alpha(\Delta K)$ which occurs with increasing coverage is again a modulation in the functional form and not a uniform increase in magnitude. Thus, we can rule out the various strong interactions mentioned above, whether direct in nature or substrate-mediated, because they all overestimate the correlation between different CO molecules.

Although all of the interactions mentioned above were too strong and led to spurious CO–CO correlation, weaker pairwise models are also incapable of reproducing the dynamics we observe. This point can be clearly demonstrated by gradually reducing the magnitude of either of the three models discussed above. For each of these completely different models, the same effect is seen; once the magnitude of the interaction model is sufficiently small to avoid the correlation features, it also becomes coverage-independent; that is, the $\alpha(\Delta K)$ do not increase in magnitude within the experimental coverage range. Thus, pairwise interactions, regardless of their strength and functional form, cannot simultaneously account for the uncorrelated nature of the CO motion and the increase in the mobility rate with increasing coverage.

The pairwise interactions, which are ruled out by the lack of CO–CO correlation, are the only coverage-dependent features in the SPI model. To explain the coverage-dependent CO hopping rate, we need to describe the system beyond the SPI approximation. The clue is found in Arrhenius plots of the measured temperature dependence of α , presented in Figure 3a, which reveal the mechanism underlying the coverage-dependent mobility. As the CO coverage increases from 0.065 to 0.3 ML, the activation energy is reduced from 175 ± 15 to 115 ± 15 meV. This reduction in activation energy, consistent with the previous macroscopic diffusion measurements,²¹ tells us that as the coverage increases, the effective PES becomes significantly less corrugated, which in turn leads to an increased hopping rate.

In order to quantify the coverage dependency of the effective PES, we return to the MD simulations. This time, the SPI approximation is circumvented by allowing the PES to vary as a function of the total coverage. [Generally speaking, if we do not assume the SPI approximation, the friction coefficient, η , may also vary with coverage. However, the reduction of the activation energy described in the text strongly suggests that the dominant change arises from the PES. Thus, to avoid an

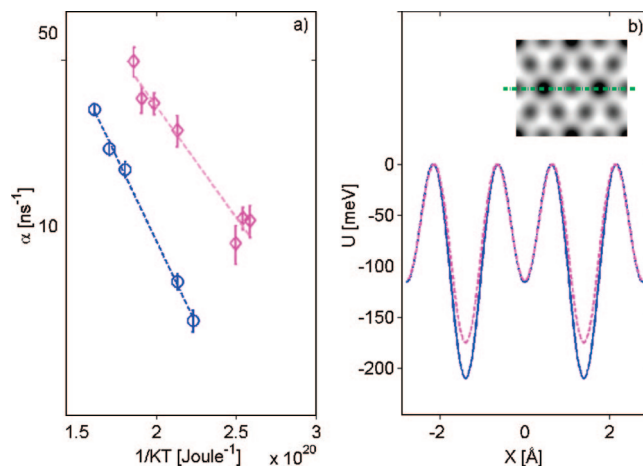


Figure 3. (a) Temperature dependence of α , measured at $\Delta K = 0.6 \text{ \AA}^{-1}$. The blue circles and the magenta diamonds were measured for $\Theta = 0.065$ and 0.3 ML, respectively. The dashed lines (blue and magenta) are the Arrhenius fits to the data mentioned in the text. (b) Coverage-dependent PES used to fit the data. The solid and dashed lines ($\Theta = 0.065$ and 0.3 ML, respectively) are the values of the PES, along the line which connects two top sites, as illustrated on top of the PES by using a green dash-dot line in the inset plot above. To allow a simple comparison, the height of the PES at the maximum is arbitrarily fixed at zero for both coverages. In reality, the changes in the heat of adsorption⁵ mean that the two curves will also be shifted apart.

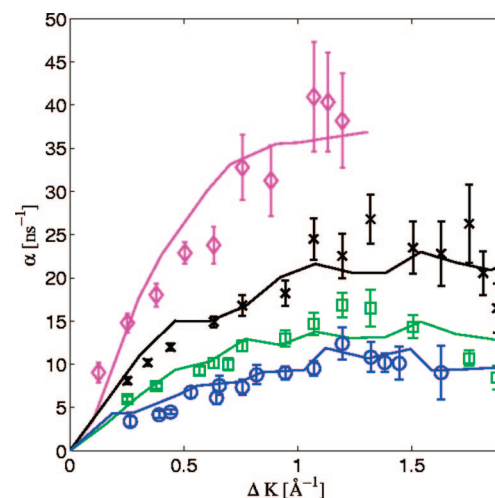


Figure 4. MD simulation results obtained by using a coverage-dependent PES. The markers show the experimental inverse lifetimes shown in Figure 1. The lines show the simulation results obtained by using a coverage-dependent PES. For CO coverages $\Theta = 0.065, 0.165, 0.22,$ and 0.3 ML, the barrier to diffusion between top sites, U_{TT} , is 210, 203, 190, and 172 meV, and the energy difference between bridge and top sites, $U_B - U_T$, is 95, 80, 70, and 60 meV, respectively. Note that the corrugation values are $\sim 30\%$ higher than the measured activation, demonstrating the nontrivial relation between the two properties³¹ and the importance of using MD simulations to analyze the dynamics.

additional free parameter, the friction is taken as coverage-independent.] The solid lines, which follow the experimental markers in Figure 4, were simulated by using a PES which changes as a function of coverage and without including any pairwise forces. Both the coverage-dependent $\alpha(\Delta K)$ curves and a 50 meV reduction of the activation between the lowest and

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highest coverages are reproduced by simultaneously reducing U_{TT} and $U_{\text{B}} - U_{\text{T}}$ as coverage increases. The optimal coverage-dependent PES is illustrated in Figure 3b. Thus, reducing the barrier to diffusion while simultaneously reducing the energy difference between the two sites reproduces all the main features seen in the data.

We note that the reduction of $U_{\text{B}} - U_{\text{T}}$ required to reproduce the ΔK dependence of α as the coverage increases also leads to a monotonic increase in the occupancy of the bridge site relative to the top site, starting from $\sim 10\%$ at 0.065 ML and reaching $\sim 30\%$ at 0.3 ML. These simulated changes in occupancies are consistent with X-ray occupancy measurements performed at slightly lower temperatures³² and do not require the existence of the strong repulsive pairwise CO–CO forces used previously to explain the site occupancy changes.⁷

Although we have shown that pairwise forces will not reproduce the coverage dependency of the microscopic dynamics, sufficiently weak pairwise forces between CO molecules may still exist without contradicting the observed dynamics. The shaded area in Figure 2a marks a region of purely repulsive interactions that do not cause significant $\alpha(\Delta K)$ modulations; that is, any coverage dependency of the $\alpha(\Delta K)$ shape produced by interactions within the shaded region is smaller than the experimental uncertainty. Thus, these weaker interactions can be included in our coverage-dependent PES simulations, without affecting the quality of the fit to the experimental data.

We note in particular that the interaction in the model proposed by McEwen et al., which was capable of explaining a large body of experiments within the SPI approximation, is approximately an order of magnitude higher than the strongest interaction that is consistent with the dynamics we observe. Figure 5 illustrates the impact of overestimating the strength of pairwise interactions. The two curves represent histograms of the nearest-neighbor distance calculated from MD simulations. The red curve was calculated for the McEwen interaction. The green curve was calculated for the strongest R^{-3} interaction which lies within the dashed region in Figure 2, that is, for a weaker interaction which does not result in correlations, which contradicts the experimental $\alpha(\Delta K)$ shape. The probability of two molecules approaching each other is significantly different for the two cases and will play a critical role in processes where adsorbate proximity is important; for example, in surface-assisted chemical reactions.

Discussion and Conclusions

Our measurements of the microscopic CO diffusion on Pt(111) reveal that the CO hopping rate between adsorption sites increases significantly with coverage. Surprisingly, the enhanced mobility is not accompanied by CO–CO correlations; that is, the motion at higher coverages is faster but remains a simple uncorrelated jump diffusion of individual CO molecules. The lack of correlation rules out pairwise CO–CO forces as the underlying mechanism for the increased mobility and reveals dynamics that cannot be explained within the SPI approximation.

By using numerical simulation, we studied a variety of generic interaction models that were used in the past to explain macroscopic CO/Pt(111) measurements. In addition to the fact that these models, like any other pairwise interaction, cannot reproduce the increase in uncorrelated hopping, our calculations

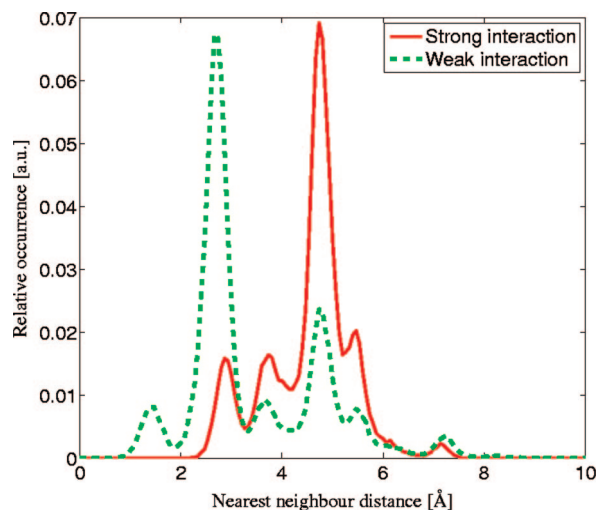


Figure 5. Illustration of the effect of lateral repulsion on the proximity of neighboring adsorbates. The two curves show normalized histograms for the distance to the closest neighbor. The histograms were calculated from simulated MD trajectories at $T = 340$ K and $\Theta = 0.17$ ML. The red curve was derived from a simulation of the R^{-3} fit to the McEwen interaction (labeled strong) mentioned in the manuscript, whereas the green curve plots the results for an upper-limit R^{-3} repulsive interaction, which is still consistent with the uncorrelated dynamics we observe, that is, lies within the shaded region of Figure 2a. As is clearly seen from this comparison, the stronger interaction strongly reduces the occurrence of close proximity between adsorbates and hence will play an important role in processes that are sensitive to this distance.

show that they significantly overestimate the correlation between CO molecules and hence are not applicable to CO/Pt(111) within the coverage range of our experiment. It is important to emphasize that the failure of the pairwise models does not contradict previous experimental observations, such as the reduction of the heat of adsorption with increasing coverage. It does, however, highlight the failure of the standard SPI approximation, which was assumed when interpreting the earlier data. The observed absence of strong repulsive forces can be reconciled with the reduction of the heat of adsorption only if the latter is not simply a function of the distance between a molecule and its nearest neighbors. This is in particular true if the heat of adsorption of a particular molecule is determined by the positions of many more adsorbates, that is, the coverage dependency of the adsorption energy is related to a nonlocal coverage, averaged over distances considerably greater than the nearest neighbor spacing. In such a situation, moving one of the neighboring molecules does not necessarily result in a force, and our observations are consistent with the previous adsorption measurements.

Our temperature-dependence measurements reveal a reduction in the activation energy of the hopping process with increasing coverage. This observation and our quantitative analysis show that the dynamics of this system can be modeled by an effective PES, which becomes less corrugated as the coverage increases. Hence, the many-body nature of CO/Pt(111) manifests itself as a coverage-dependent mean field, which on the one hand renormalizes the PES and modifies the CO hopping rate and yet allows the CO molecules to move in a practically uncorrelated way. The origin of this mean-field effect and the reasons that lead to the breakdown of the SPI interaction are yet to be determined and, given the long-range nature of the problem, presents a challenging theoretical task.

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Because very few empirical microscopic dynamics studies exist to date, we are unable to estimate whether the behavior of CO/Pt(111) is an exception or whether the validity of the SPI model is more restricted than previously believed. Further ^3He spin-echo measurements of other surface systems, which exhibit coverage-dependent adsorption properties, are planned to answer this question. For example, a similar coverage dependence of the macroscopic properties has been seen for $\text{NH}_3/\text{Re}(001)$.³³ These results have been successfully modeled by using long-range pairwise interactions,³⁴ making future experiments and calculations of the microscopic diffusion properties particularly interesting. Finally, the present study

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highlights the importance of atomic scale dynamics measurements as a sensitive probe for measuring interadsorbate forces.

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Supporting Information Available: Signatures of pairwise interaction in the ISF and experimental and numerical details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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