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Large Entropy Difference between Terrace and Step Sites on Surfaces

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Abstract: Using atomic beam/surface scattering measurements to investigate the desorption kinetics of low-coverage Pb from Mo(100), we uncover a large entropy difference between Pb atoms at terrace and step sites, which should be general for adsorbates on surfaces at high temperatures. A line shape analysis of the transient desorption signal reveals the presence of two species with different lifetimes on the surface. An Arrhenius analysis of these lifetimes from 1150 to 1320 K provides the prefactors and desorption activation energies (332 and 411 kJ/mol) of these two states. A comparison of these energies to those measured directly via adsorption calorimetry strongly suggests that one state is a terrace-bound species. The other, more strongly bound species is attributed to steps. The more strongly bound step species has the higher rate constant for desorption because of its much larger desorption prefactor (9×10^{19} vs $5 \times 10^{15} \text{ s}^{-1}$). Within transition state theory, the ratio of these prefactors corresponds to 82 J/(mol K) higher entropy for the terrace species than for the step species. This large entropy difference is quantitatively reproduced by a simple model which assumes the terrace species is a 2D ideal gas parallel to the surface and the step species is a 1D ideal gas along the step edges. Such a difference will generally exist for adsorbed species when $k_B T$ exceeds the barrier height for adsorbate diffusion across terraces. A consequence of this large entropy difference is that the defect sites are much less populated relative to terrace sites than would be expected based on enthalpy alone. The measured prefactor for Pb desorption was used to analyze earlier surface lifetime measurements for Pb on MgO(100) to extract adsorption energies for that system, as well.

Introduction

The desorption of a molecule or atom from a surface is a fundamentally important step in many technologically and biologically relevant reactions. Desorption rates play an especially strong role in catalysis since they may directly determine a reaction's turnover frequency through governing the rate of reaction product release or the lifetime of reactants, intermediates, or inhibitors on the catalyst's surface. Within an Arrhenius model, desorption kinetics are characterized by an activation energy for desorption, E_{des} , and a prefactor, ν_0 , which provide the rate constant for desorption, k , through $k = \nu_0 \exp(-E_d/k_B T)$.¹ Differences in experimentally observed desorption rate constants are most often attributed to differences in E_{des} while assuming a constant value of 10^{13} s^{-1} for ν_0 . This assumed value arises from transition state theory along with the notion that the adsorbed state and transition state are similar in nature such that the ratio of their partition functions is nearly one.² When the adsorbed and transition states are not alike, values of ν_0 can differ by orders of magnitude from 10^{13} s^{-1} .^{3,4} In these situations, the prefactor may become the dominant factor determining the relative rates of desorption of various species from a surface. This could lead to the observation of somewhat

counter-intuitive phenomena such as a higher desorption rate constant for a state with a much higher activation energy for desorption. In this paper, we present direct experimental evidence for this phenomenon. We observe a larger desorption rate constant for a step-bound species than for a terrace-bound species, even though it is nearly 80 kJ/mol more strongly bound. This is a consequence of the lower dimensionality of the step-bound species (1D) providing a larger entropy gain as it reaches the transition state for desorption and therefore a much larger desorption prefactor compared to that of the terrace-bound species (2D).

If a surface adsorption/desorption process is nonactivated, the transition state for desorption is very late in the reaction coordinate, and the transition state is not at all like the adsorbed state, but instead closely resembles the desorbed product. A common example is an adsorbed state that is a localized oscillator in a site at temperature T , but which has a desorption transition state best characterized as a 2D gas far enough from the surface to no longer feel any attraction. In this case, the two vibrational degrees of freedom parallel to the surface of the localized adsorbate are converted into translational degrees of freedom in the transition state. Since translational degrees of freedom contribute much more than vibrational degrees of freedom to their respective partition functions (often by orders

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of magnitude), the ratio of partition functions of the activated state to adsorbed state greatly exceeds unity, giving rise to a prefactor far exceeding 10^{13} s^{-1} .⁵ Fair and Madix have used this argument to explain prefactors for CO desorption from metal surfaces that can reach values as high as 10^{18} s^{-1} .⁵ This has been supported by later observations.^{3,4} Since it is the ratio of partition functions of the transition state to the adsorbed state that determines the prefactor for desorption, the restriction of a localized adsorbate, while providing an easily visualized example, is not necessary in order to account for large desorption prefactors but only that the transition state and adsorbed state differ significantly in entropy.

In this paper, we have studied the desorption of Pb atoms from a Mo(100) surface at low coverage ($\sim 0.015 \text{ ML}$) for temperatures between 1100 and 1320 K using pulsed atomic beam/surface scattering measurements, which previously have been extremely successful in providing detailed analysis of the dynamics of processes occurring on surfaces.^{6–11} Through analysis of desorption transients, the present experiments provide a direct measure of the lifetime of the Pb atoms on the surface. We observe desorption from two states. By comparing the extracted desorption activation energies to adsorption energies measured directly via single-crystal adsorption calorimetry,¹² the two states are consistent with Pb adsorbed on the Mo(100) terraces and step edges for the more weakly and strongly bound species, respectively. Further, this adsorption system is nonactivated. This implies an unbound desorption transition state located at relatively large distances from the surface and suggests that this system will display the large desorption prefactors we observe. At the temperatures in this study, the more strongly bound step species has the higher rate constant for desorption and is the dominant species desorbing from the surface. Our observations can be explained by comparing the properties of a 1D gas confined along the step edges for the more strongly bound step species to those of a 2D gas on the terraces for the more weakly bound species, with similar desorption transition states for the two species. The lower entropy of the 1D gas, compared to that of the 2D gas, leads to a larger gain in entropy as it passes through the transition state, resulting in a larger prefactor for desorption and in turn a larger desorption rate constant. Using a simple model, we have simulated the data. In these simulations, while there is incident Pb gas flux on the surface, equilibrium between the terrace and step sites provides Pb to the step sites from which the Pb atoms more rapidly desorb. This results in the step sites contributing more to the simulated Pb desorption than the more abundant terrace sites even though they cover only $\sim 1\%$ of the surface and the Pb being $\sim 80 \text{ kJ/mol}$ more strongly bound at the step edges.

Previous modulated molecular beam measurements performed at low adsorbate coverages for other adsorbates and other stepped surfaces have similarly observed a greater contribution of steps to desorption than terraces.^{13–15} Typically, this has been

attributed to a greater concentration of adsorbates at the step sites due their higher adsorption enthalpy compared to that of terrace sites. However, our data can be accurately simulated with larger Pb populations on the terraces, along with large differences in entropy between step and terrace sites, which lead to large differences in desorption prefactors. A consequence of this is that desorption from the more strongly bound steps still dominate desorption from surfaces at low coverages, but this is *not* due to a higher equilibrium adsorbate amount at step sites. Instead, it is because the step sites have a higher rate constant for desorption than the terrace sites due to the difference in desorption prefactors. These results imply that there is generally a higher relative concentration of adsorbates at terrace sites on stepped surfaces at low coverage than previously thought. Thus, low coverage chemical transformations (for example, catalysis) on such surfaces are not as dominated by step site behavior as previously expected (based on enthalpy considerations alone).

Experimental Section

The experiments were performed in an ultrahigh vacuum (UHV) chamber with base pressures of $<10^{-10}$ Torr, described previously.¹⁶ The $1 \mu\text{m}$ thick Mo(100) single crystal was cleaned via repeated cycles of oxidation followed by annealing in vacuum until no impurities could be detected with Auger electron spectroscopy and a sharp (1×1) LEED pattern was visible.¹² For the measurements presented here, the sample was brought to a constant temperature, then pulses of Pb gas from a chopped effusive metal atom source were directed nearly normal to the surface. The source flux during these measurements was $1.4 \times 10^{14} \text{ atoms/cm}^2/\text{s}$, measured with a quartz crystal microbalance (QCM), and was chopped into 100 ms pulses of Pb atoms at $1/2 \text{ Hz}$ containing 0.014 ML . One ML is defined as the Mo(100) atomic density ($1.01 \times 10^{15} \text{ atoms/cm}^2$). Pb atoms desorbing from the surface ($m/e = 208$) were detected with a quadrupole mass spectrometer (QMS, UTI) in line-of-sight to the Mo(100) surface placed at the magic angle, 57° , from the surface normal.¹⁷ The Mo(100) crystal was heated via electron bombardment on the back side of the crystal, and its temperature was calibrated using optical pyrometry.

Results and Discussion

Figure 1 presents the QMS signal intensity ($m/e = 208$) as a function of time, $s(t)$, for temperatures ranging from 1100 to 1320 K during the first 0.75 s of a desorption trace. In general, it is evident that as the temperature decreases the lifetime of the Pb atoms on the surface increases, resulting in a longer decay time in the QMS signal. We have calculated the QMS signal expected for Pb atoms having zero lifetime on the surface, the instrument response function $i(t - t')$, using known system parameters such as the atomic beam diameter, atomic beam chopper blade geometry, its rotational speed, and the beam position on the chopper as its opening rotated through the beam. The desorption traces in Figure 1 are a convolution of $i(t - t')$ and a system response function, $h(t')$, that represents any physical process leading to a time lag of the Pb atoms on the Mo(100) surface.¹¹

$$s(t) = \int_0^\infty i(t - t')h(t')dt'$$

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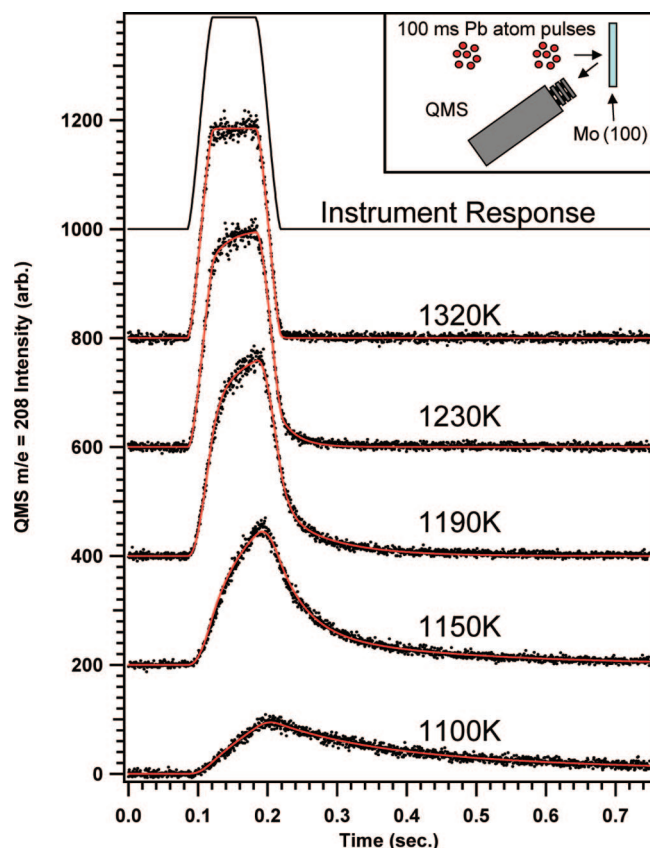


Figure 1. Observed Pb QMS signal (at $m/e = 208$) as a function of time for 100 ms pulses at $\frac{1}{2}$ Hz of Pb atoms onto a Mo(100) surface at various temperatures. The data points are averages of 25 measurements. The red lines are fits to the data assuming desorption from two distinct and independent states.

In order to accurately determine the Pb atom's lifetime on the surface, the system response function must be deconvoluted from the instrument response.

In the simplest case, the desorbing Pb atoms arise from a single state and the desorption process is first-order. Then, the system response function will be represented by an Arrhenius expression which decays exponentially with time, or $h(t) = Ae^{-t/\tau}$. In this expression, τ is the characteristic lifetime of Pb atoms on the surface (or surface residence time) and equals the inverse first-order rate constant for desorption $\tau = k^{-1} = \nu_0^{-1} \exp(E_{\text{des}}/k_B T)$.¹ Thus, by plotting $\ln \tau$ versus $1/T$, it is possible to extract E_{des} and ν_0 from the slope and y-intercept, respectively. We have attempted to fit our observed QMS decay curves assuming this single state model, but the resulting fit was poor.

The decay curves were well fitted, however, with an expression for the system response function, $h(t)$, that would be appropriate if the observed signal arises from the desorption of two distinct and independent species with different surface residence times. In this case, the system response function is simply the sum of two exponential decay functions each with different surface residence times and weighting factors (A_1 and A_2), or $h(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}$. The temperature dependence of the two surface residence times is assumed to behave in an Arrhenius manner each with its own desorption activation barrier and prefactor. The resulting fits are included in Figure 1 where it is seen that this functional form fits the data quite well. The fitting parameters are summarized in Table 1, columns 2–5. The ratio $A_1 \tau_1 / A_2 \tau_2$ is equal to the ratio of the total time-

Table 1^a

T (K)	A_1	A_2	τ_1 (ms)	τ_2 (ms)	$(N_1/N_2)_{\text{fit}}$	K_{eq} (m^{-1})	$(N_1/N_2)_{\text{eq}}$	$(N_1/N_2)_{\text{sim}}$
1320	0.064	1.63	2.7	0.2	0.53	2.25×10^8	8.5	0.62
1230	0.0054	0.155	25	2.4	0.36	1.29×10^8	4.9	0.64
1190	0.0021	0.029	78	17	0.33	9.79×10^7	3.7	0.84
1150	0.0010	0.0068	232	41	0.83	7.28×10^7	2.75	1.35
1100	0.00060	0.0010	483	136	2.13			

^a Fit parameters extracted from the desorption traces shown in Figure 1 (columns 2–5). See text for parameter description. Columns 7 and 8 provide the calculated equilibrium constants used in the simulations and the calculated surface population ratios using these equilibrium constants. Column 9 provides the ratio of the number of atoms desorbing from terrace sites and step sites from the simulated data. Species 1 is attributed to Pb atoms desorbing from terrace sites and species 2 from step sites on the Mo(100) surface.

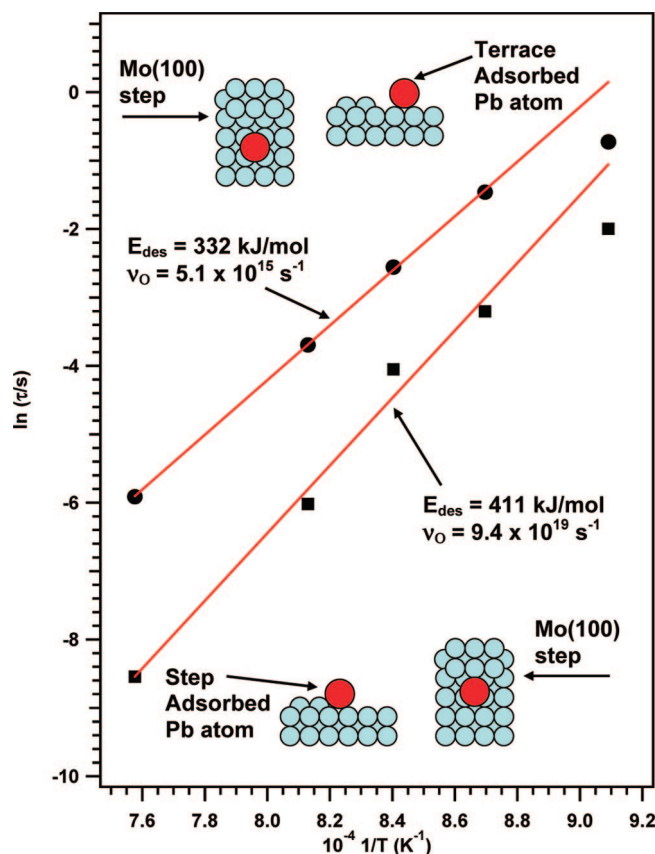


Figure 2. Arrhenius plots using the parameters extracted from the desorption trace fits shown in Figure 1. Indicated are the desorption activation barriers and prefactors for the two adsorbed states observed.

integrated contributions of species 1 and species 2 to the entire pulse area, which separates into two integrals, one for each species. These ratio values are also included in Table 1 and listed as $(N_1/N_2)_{\text{fit}}$. At temperatures down to 1150 K, this ratio is less than 1, implying that state 2, the species with the shorter lifetime on the surface, contributes more to the desorption trace and at short times is the dominant species desorbing from the surface. Using the values of $(N_1/N_2)_{\text{fit}}$ and the known total amount of Pb in a single pulse (0.014 ML), we can estimate that species 2 arises from sites that cover approximately 1% of the surface assuming that all of these sites are saturated at the end of a Pb pulse.

Figure 2 shows the corresponding Arrhenius plots with linear fits for the values extracted from the fits to the desorption traces in Figure 1. The lowest temperature points (1100 K) were not

included in the linear fits. The reason for not including these points was that the integrated area under the 1100 K desorption trace was 22% lower than the area under the other curves which showed the same integrated area within statistical error. This indicates that, at 1100 K, ~22% of the Pb atoms have a longer residence time on the surface than the chopper period of 2 s, causing a buildup of Pb on the surface. Thus the 1100 K desorption trace is not representative of isolated Pb atoms on the Mo(100) surface but represents desorption from a Mo(100) surface with a finite Pb coverage. The Arrhenius plots for the best fits to the four higher temperature data points give desorption activation barriers of 332 ± 4 and 411 ± 35 kJ/mol and desorption prefactors of $(5.1 \pm 0.2) \times 10^{15}$ and $(9 \pm 3) \times 10^{19} \text{ s}^{-1}$ for the minor (species 1) and dominant species (species 2), respectively. The errors reported here are errors from the linear fits of the Arrhenius plots.

If adsorption is a nonactivated process (as implied by the measured unit sticking probability at 300 K for this system¹²), the desorption activation energy should be equal to the adsorption energy^{2,18} (i.e., the forward activation energy minus the reverse activation energy equals the net reaction energy). In a previous study, we have measured the adsorption energy versus coverage of Pb atoms on this same Mo(100) surface at 300 K directly with single-crystal adsorption microcalorimetry.¹² In that study, the initial (zero coverage) adsorption energy of 335 kJ/mol was attributed to terrace (100) sites for three reasons: (1) terrace sites comprise ~99% of this surface (see below); (2) the rule of thumb that the diffusion activation barrier is 1/5 to 1/2 of the adsorption energy predicts that diffusion is too slow at 300 K for most Pb atoms to diffuse to the 1% step sites on the ~100 ms time scale of the heat measurement; (3) this lack of mobility was supported by the shape of the measured adsorption heat versus coverage curve, which decreased strongly and smoothly with coverage but showed neither a markedly higher heat at very low coverage that could be attributed to the selective population of more strongly binding steps nor the sigmoidal shape it would have had if the adsorbates were mobile at 300 K and thus could diffuse into their energetically preferred state (i.e., further apart than random, to minimize repulsions). Instead, it was well-fitted by a second-order polynomial, any model for which requires immobile adsorbates with lateral repulsions. This initial calorimetric adsorption energy for terrace sites agrees very well with the lower valued desorption barrier (332 kJ/mol) measured in the present study, so we will also attribute the latter to Pb at terrace sites for the remainder of this paper. Of course, in the absence of direct proof that terrace sites are indeed being populated initially on the 100 ms time scale of the calorimetry experiments, we cannot be completely sure of the site assignment in that calorimetry study. Also, the fact that the lower desorption energy here equals the initial calorimetric energy does not completely prove that the same sites are being populated in both cases. We make this assignment because it is the simplest model that is consistent with all the known data for this system.

Assuming that this value of 332 kJ/mol is indeed associated with the adsorption of a Pb atom into the 4-fold hollow sites on a Mo(100) terrace (species 1), we obtain a value of $332/4 = 83$ kJ/mol for the average Pb–Mo bond energy for each of Pb's four nearest-neighbor bonds. A Pb adatom at a step edge on this BCC(100) surface would have one additional Pb–Mo bond

(see Figure 2), so we can estimate its adsorption energy as five times this Pb–Mo bond energy, or 415 kJ/mol. This is very close to the second desorption energy of 411 kJ/mol measured here (species 2), indicating that species 2 most likely arises from Pb adatoms at steps. Importantly, our results indicate that this more strongly bound step species has a higher rate constant for desorption (shorter lifetime on the surface) than the more weakly bound species at all temperatures of the present study. This must be a result of drastically different desorption prefactors for the terrace- and step-bound species.

The values obtained from the Arrhenius plots indicate that the desorption prefactor for the step-adsorbed atom is 1.8×10^4 times that of the terrace-adsorbed atom's prefactor. Assuming similar transition states for desorption from the steps or terraces, the difference in prefactors would arise from differences in the adsorbed states. Within transition state theory, these prefactors are related to the entropy change associated with going from the adsorbed initial state to the transition state. Assuming that the transition state is the same for both species (essentially a 2D ideal gas some distance from the surface), we can calculate a difference in entropy between the step- and terrace-adsorbed species via $\nu_{\text{O,step}}/\nu_{\text{O,terrace}} = e^{\Delta S_{\text{step}}/k_B}/e^{\Delta S_{\text{terrace}}/k_B} = 1.8 \times 10^4$, providing a value of $\Delta S_{\text{terrace}} - \Delta S_{\text{step}} = 9.8k_B = 81.5 \text{ J/(mol K)}$, where k_B is Boltzmann's constant.² At the temperatures of this study, 1100 to 1320 K, this corresponds to a difference in the entropic contribution to the free energy of 90 to 108 kJ/mol, which is sufficient to overcome the difference in desorption energies of 79 kJ/mol. Therefore, entropy is the dominant factor determining the relative desorption rate constants for Pb atom desorption from step and terrace sites on the Mo(100) surface. An additional important consequence of this difference in entropy (which is also born out in the simulations below) is that the defect sites are not nearly as heavily populated (relative to terraces) as would be expected based on enthalpy alone at these high temperatures since entropy favors terrace (2D) population over step (1D) population. Here we examine step sites as the defect, but this entropic effect should be even stronger at point defects, which have lower entropy than steps since the adsorbate is a localized oscillator.

As a first approximation to model this system, we assume that, at these high temperatures, the Pb atoms adsorbed on the terrace exist as a 2D gas parallel to the surface and that the Pb atoms at the step sites exist as a 1D gas (i.e., their diffusion barriers across terraces and along steps, respectively, are small compared to $k_B T$, where T is temperature). For simplicity, we also assume that the vibrational partition functions of the terrace 2D gas (i.e., the oscillator in the direction perpendicular to the surface) and the step 1D gas (i.e., the two oscillators in the directions perpendicular to the surface and perpendicular to the steps but parallel to the surface) are unity. That is, we assume that only their ground states are populated in these vibrational modes. Within this model, the difference in entropy between the step and terrace species can be calculated as the difference in entropy between a 1D and 2D gas^{19,20}

$$\Delta S_{2D} - \Delta S_{1D} = \frac{k_B}{2} + k_B \ln \left[\frac{A}{L} \left(\frac{2\pi m k_B T}{h^2} \right)^{1/2} \right] \quad (1)$$

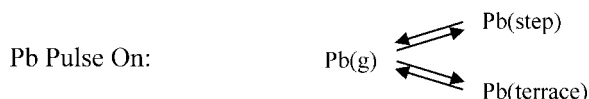
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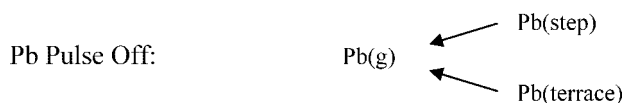
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where m is the mass of a Pb atom, h is Planck's constant, and A/L is the inverse step density (inverse step length per unit area). Using a value of $A/L = 3.78 \times 10^{-8}$ m, corresponding to 0.8% ML step density, gives $\Delta S_{2D} - \Delta S_{1D} = 9.8k_B$, the same value found using the ratio of prefactors extracted from the Arrhenius plots of Figure 2. Note that this assumes a value for the step density very similar to that implied from the population ratios of the fits as discussed previously ($\sim 1\%$).

Since the measured pulses nearly reach constant intensity during the beam-on time at these high temperatures (indicating their approach to a constant rate of desorption), both site populations must be approaching their equilibrium values. Thus, the incident gas phase flux helps ensure the establishment of equilibrium between the terrace and step atoms while the Pb pulse is on, that is



However, when the flux is off, this is no longer a valid assumption since the Pb is rapidly depleted from the surface and there is no incident gas phase Pb to replenish it. This would imply that, once the incident Pb flux is off, the Pb desorbs from the surface more as Pb desorbing from independent sites than



when the pulse is on. That is

During the adsorption phase (when the beam is on), the terrace and step sites reach equilibrium through the fact that they are both populated to equilibrium from the gas phase and the time is long (0.1 s). However, diffusion between step and terrace sites is not rapid on the shorter time scale probed in the step site desorption transients here (~ 0.05 – 0.0002 s). Most likely, the steps and terrace species are not in complete equilibrium when the pulse is on (the incident Pb lands mostly on terrace sites, which may increase the terrace population slightly above its equilibrium value) or completely independent when the pulse is off (diffusion may supply further Pb to the step sites after some Pb has desorbed during the pulse off period). However, we have used this simple model to simulate the pulse lineshapes of Figure 1 from 1150 to 1320 K, assuming that the atoms at steps and terraces are in equilibrium while the pulse is on, but that the step and terrace Pb atom populations decay independently once the Pb atom pulse is off.

Following Hill,²⁰ we can derive an equilibrium constant describing the equilibrium ratio of the coverages, θ , of the terrace sites (atoms per unit area) to the step sites (atoms per unit length) assuming again that they exist as 2D and 1D gases on the surface, respectively.

$$K_{\text{eq}} = \frac{\theta_{\text{Terr}}}{\theta_{\text{Step}}} = \frac{N_{\text{Terr}}/A}{N_{\text{Step}}/L} = \left(\frac{2\pi mk_B T}{h^2} \right)^{1/2} \exp \left[\frac{-(E_{\text{Ads}}^{\text{Terr}} - E_{\text{Ads}}^{\text{Step}})}{kT} \right] \quad (2)$$

Using $E_{\text{Ads}}^{\text{Terr}} = 332$ kJ/mol and $E_{\text{Ads}}^{\text{Step}} = 411$ kJ/mol from the fits to the data, Figure 2, the values of K_{eq} for the temperatures in this study can be calculated. These values are listed in Table 1. The values of K_{eq} indicate that at equilibrium the concentration of Pb atoms on the terraces is larger than the concentration of Pb atoms at the steps. Multiplying this K_{eq} by the value $A/L =$

3.78×10^{-8} m provides the ratio of the number of atoms in terrace sites to the number of atoms in step sites when they are in equilibrium, $(N_1/N_2)_{\text{eq}}$. We also list these equilibrium ratios in Table 1. $(N_1/N_2)_{\text{eq}}$ is always larger than $(N_1/N_2)_{\text{fit}}$ because atoms on the terraces have a smaller desorption rate constant and desorb more slowly, therefore contributing less to the total time-integrated desorption signal and decreasing the value of $(N_1/N_2)_{\text{fit}}$. The values of the ratios $(N_1/N_2)_{\text{fit}}$ and $(N_1/N_2)_{\text{eq}}$ also approach each other as temperature decreases and their rate constants converge (as in Figure 2), for these same reasons.

The time increment used in the simulations was 0.5 ms. Starting at the leading edge of the incident Pb pulse, the amount of Pb per 0.5 ms step incident on the surface is calculated using the instrument response function (see Figure 1) and the measured total amount of Pb in the pulse. This amount of Pb is then split between the terrace sites and step sites using the equilibrium ratio calculated from eq 2. The amount of Pb desorbing from the step sites and terrace sites during the next 0.5 ms is then calculated using the rate constants found from the fits to the data, Figure 2. Following this, the amount of Pb incident in the pulse is again calculated, and this amount is added to the amount that remains on the surface, and this total amount of Pb is divided between step and terrace sites using eq 2. The amount of Pb desorbing from each site is then calculated for the next 0.5 ms, and the process is repeated until the end of the incident Pb pulse. Once the pulse is off, the populations of the terrace and step sites are allowed to decay independently, again using the same rate constants as when the Pb pulse was on. The resulting simulated curves were scaled so that their area was the same as the area under the measured decay curves. Results of the simulation along with a comparison to the experimental data are shown in Figure 3a–d. The simulations reproduce the time and temperature dependence of the data and demonstrate that the above simple model is consistent with the experimental results.

In Figure 3e–h, the simulated data are separated into the contributions from the step sites (blue) and terrace sites (green). As expected from its higher desorption rate constant, desorption from the step sites increases more rapidly than terrace site desorption while the pulse is on and decays more rapidly when the pulse is off. These simulations have assumed that the terrace and step species desorb entirely independent of each other after the beam is off, and indeed their population ratio quickly increases well above its equilibrium value after the beam is off since terrace desorption becomes the dominant portion of the signal. Thus, during the beam-off decay period, surface diffusion from terraces to steps is not fast enough to maintain equilibrium concentrations of Pb at the steps to keep up with the faster rate of step desorption. When the beam is on, however, the incoming gas ensures that these site populations reach their equilibrium ratio with the result that, while the beam is on, the dominant species desorbing from the surface at all temperatures in this study is the more strongly bound step species as indicated by the higher intensity of the blue curve compared to the green curve.

In addition, these simulations reproduce the observation that for temperatures above 1190 K the step species is on average the dominant species desorbing from the surface for the entire desorption trace as indicated by the larger area under the blue curve than the green curve. We have quantified this by calculating the ratio of the total integrated area under the terrace site curve (green) to the step site desorption curve (blue) and listed the results as $(N_1/N_2)_{\text{sim}}$ in Table 1. These values agree well with the experimental ratios, $(N_1/N_2)_{\text{fit}}$, in that they are less

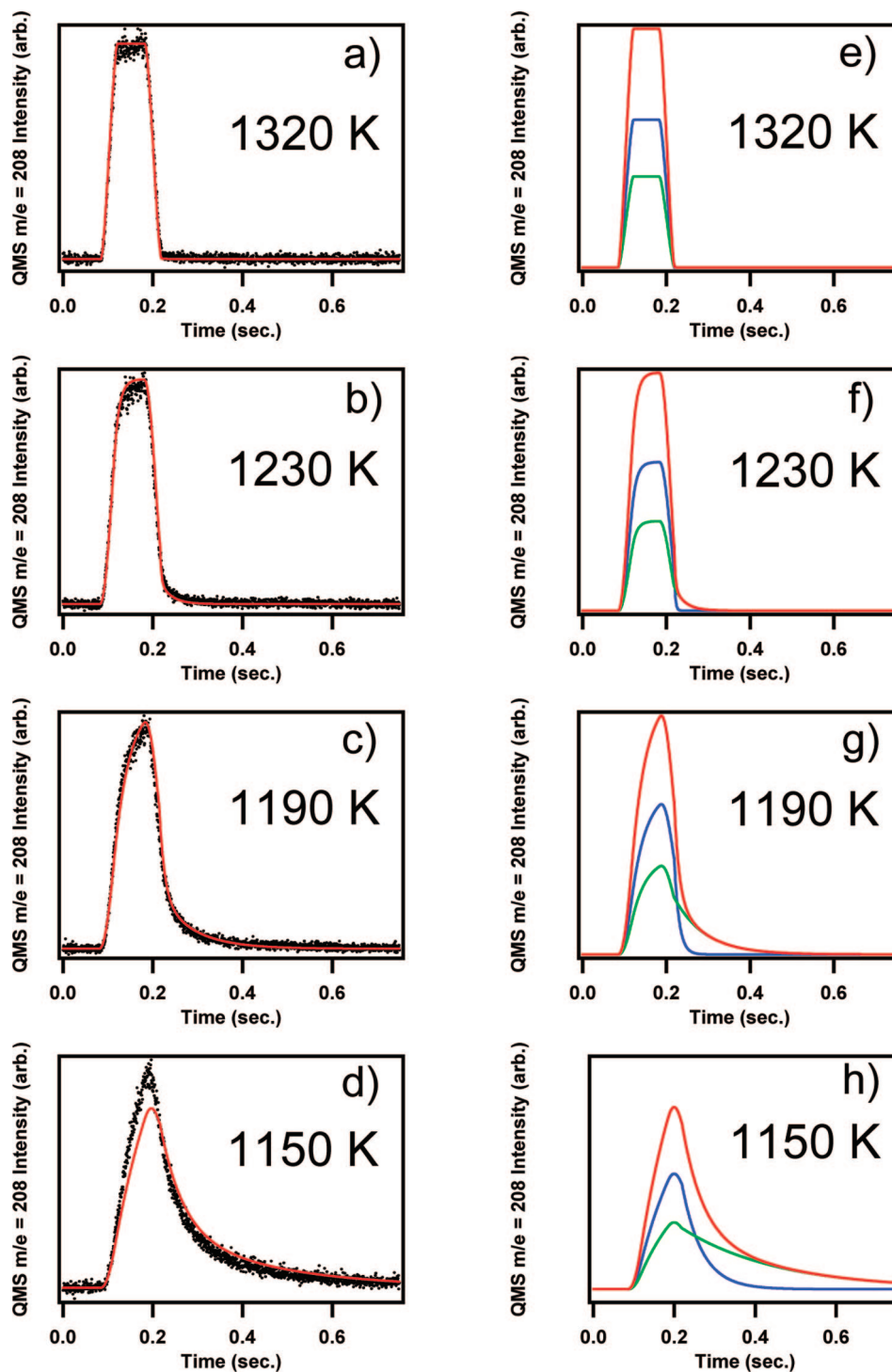


Figure 3. Data and simulations using a model assuming equilibrium between the step sites and terrace sites while the incident Pb pulse is on. (a–d) Data black dots, simulated data red line. (e–h) Simulated total signal (red) separated into contributions from step sites (blue) and terrace sites (green).

than unity and nearly independent of temperature. For temperatures above 1190 K, these values are all slightly less than 1, indicating that the step-bound species is the dominant species desorbing from the surface for the total desorption trace. The simulation for the 1150 K data has the strongest deviation from the experimental data, Figure 3d, and the direction of deviation is such that the contribution from the steps is underestimated, indicating that even at 1150 K the step-bound species may still be the dominant desorbing species.

The results of the simulations indicate that, for the Pb/Mo(100) system at temperatures above 1150 K, the system can

be adequately described as a surface composed of both a 1D gas for the Pb atoms confined along the step edges and a 2D gas for the Pb atoms existing on the terraces, wherein these are in equilibrium when there is incident Pb flux onto the surface. In addition, desorption from the more strongly bound step sites is more rapid (larger rate constant) due to its higher entropy gain as it approaches the transition state compared to the terrace sites. This difference in entropy gain can be quantified by comparing the entropy of a 1D gas to that of a 2D gas and highlights the effect that dimensionality can have on relative rate constants for desorption. Our simulations indicate that Pb

atoms still predominantly desorb from step sites even though (1) step sites account for only about 1% of the sites on the surface, (2) they are less populated than would be expected based on enthalpy alone, and (3) they bind Pb atoms ~ 80 kJ/mol more strongly than terraces. This is due to the large entropy difference between the step species versus terrace species.

Previously, the observation of adsorbate desorption from surfaces at low coverage occurring predominantly from step sites has been attributed to an enthalpic effect.^{13–15} That is, on the basis of their higher adsorption enthalpies, the step sites were previously assumed to have a significantly higher concentration of adsorbates than terraces. Here we have shown that entropy essentially plays two competing roles. First it contributes to the relative populations of the terrace and step sites. Entropy favors the population of two-dimensional terrace sites over one-dimensional step sites (see values for K_{eq} in Table 1). This means that the terraces are more highly populated (and steps much less highly populated) than would be expected from pure enthalpic considerations alone. Second, entropy favors desorption from steps over terraces at high temperatures, as reflected in the large difference in desorption prefactors between the step- and terrace-bound species found here. The latter difference can be sufficient to overcome the entropically driven lower population of steps, so that steps still contribute more to the desorption signal in pulsed molecular beam measurements. Therefore, the dominance of step site desorption may not be due to a higher concentration of adsorbates at steps as previously assumed, but rather due to a higher rate constant for desorption from steps. Using the calculated rate constants, the dominance of this entropic effect disappears below 967 K when the rate constant for desorption of the more weakly bound terrace species becomes larger than the rate constant for desorption of the step species.

Typically, steps are thought to act as sinks for adsorbed species, increasing their lifetime on the surface and decreasing their rate of desorption. The results in this study, however, indicate that in some cases a few steps may decrease the average lifetime of all the adsorbed species on surfaces due to an entropic effect. One possible consequence of this is that at high temperatures, if the step sites on the surface are blocked, the average lifetime of the Pb atom on the surface will increase from lack of access to the step sites which decreases their residence time due to their larger desorption rate constant. These effects are especially pronounced when there is incident gas flux onto a surface. Our results also indicate a much higher population of terrace sites relative to defects than previously thought in studies where desorption was observed to be dominated by step sites. This may mean that terrace sites contribute more to reactions on surfaces at low coverage than has been previously considered, when steps were thought to dominate populations based on enthalpic differences alone. This result should be quite general and apply to systems when $k_B T$ is larger than the adsorbate diffusion barrier across terraces (so that it behaves as a 2D ideal gas). This applies even at room temperature for many adsorbed species. Since diffusion barriers at steps and other defects are generally larger than across terraces, this entropy difference will be even larger at intermediate temperatures when the terrace species approximates a 2D ideal gas but the species at defects is still trapped and behaves as a localized oscillator.

Similar measurements of the surface residence times of Pb atoms on an MgO(100) thin film, grown on Mo(100), at 280 K

are reported elsewhere.²¹ There we found two lifetimes: 1.6 and 88 ms. In that study, the Pb atoms that do not desorb were found to stick to 3D Pb nanoparticles which decorate only a fraction of the step edges. This indicates that the desorbing Pb adatoms visited steps during their lifetime on the surface. Using these lifetimes together with the prefactor found above for steps, we estimate adsorption energies of 92 and 101 kJ/mol, respectively. Using instead the terrace prefactor from above gives energies of 69 and 78 kJ/mol, respectively. If we assume these two lifetimes correspond to steps and terraces, we can conclude that Pb on MgO(100) has a heat of adsorption of 69–78 kJ/mol at terraces and 92–101 kJ/mol at steps, without specifying which lifetime corresponds to which type of site.

Conclusion

In summary, we have measured the lifetime of Pb atoms on the Mo(100) surface using atomic beam reflectivity measurements. The data are consistent with the presence of two different types of sites for Pb adatom sites which differ in adsorption energy by ~ 80 kJ/mol, but with more rapid desorption of the more strongly bound species at high temperatures. Comparison of the desorption activation energies measured in the present study with adsorption energies measured directly via adsorption calorimetry allows us to attribute the more weakly bound species to terrace sites and the more strongly bound species to steps. The more rapid desorption of Pb from the step sites on the Mo(100) surface as compared to terrace sites is a result of its much larger prefactor for desorption. We found desorption activation energies (adsorption energies) of 332 ± 4 and 411 ± 35 kJ/mol and desorption prefactors of $(5.1 \pm 0.2) \times 10^{15}$ and $(9 \pm 3) \times 10^{19} \text{ s}^{-1}$ for terraces and steps, respectively. This larger prefactor for the steps is due to a larger entropy gain in going from the adsorbed state to the transition state, arising from the lower entropy of a 1D gas (for the more localized step sites) compared to a 2D gas (for the more delocalized terrace sites). The reduced dimensionality of the 1D gas leads to a lower entropy in the step-adsorbed state compared to a 2D gas (terrace state) and thus results in a higher entropy gain as it approaches the transition state. This leads to the step sites having a higher rate constant for desorption than terrace sites at temperatures above 967 K. This large entropy difference between species at steps and terraces should be valid in general for surface species at high temperatures (where $k_B T$ is comparable to or larger than the diffusion barrier across terraces). Its net effect is that defect sites are not nearly as heavily populated, relative to terraces, as one would expect based on energy (or enthalpy) alone. This may have a significant influence on the interpretation of many surface processes where the relative contribution of terrace and defect sites to surface reaction rates is important.

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