Molecular dynamics simulations of desorption

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Results of classical molecular dynamics simulations at low temperature of the desorption of Xe atoms from various transition metal surfaces are presented. We use the generalized-Langevin-equation formalism and the compensating Hamiltonian method. The desorption rate constant is calculated with variational transition state theory. The effect of corrugation (Xe/Pd(100)), coverage dependence (Xe/Pt(111)), and the effect of steps (Xe/Pt(112)) are studied. A comparison with temperature-programmed desorption spectra enables us to estimate the effect of the substrate on the Xe–Xe potential, and the changes in the Xe–Pt potential at steps.

1. Introduction

Although the desorption of physisorbed atoms at low temperature is a relatively simple activated process, it is still only poorly understood. It is possible to study the desorption dynamics in detail for an ideal surface and low coverage using molecular dynamics (MD) [1,2]. If defects are present or when the coverage increases the system is much more complicated however. The difference is that one can construct reliable potential energy surfaces for the former case, but not for the latter. Little is known about the interaction with defects, and it is not clear what the effect is of the substrate on the adsorbate–adsorbate interaction.

We present results of MD studies on Xe desorption. Adsorbed Xe is interesting for its use in photoemission of adsorbed xenon (PAX) spectroscopy [3]. We have looked at the influence of the surface corrugation on the desorption from Pd(100). We have investigated the effect of substrate-induced changes in the Xe–Xe potential in Xe/Pt(111), and the effect of steps on Xe desorption from Pt(112) by comparing MD results with temperature-programmed desorption (TPD) spectra.

2. Theory

We have used the generalized-Langevin-equation (GLE) formalism as developed by Adelman [4], Tully [1], and DePristo [5]. Only a small number of substrate atoms that have a direct interaction with the adsorbed atoms is simulated. The rest of the substrate is replaced by a limited number of so-called ghost particles. Their equation-of-motion is a generalized Langevin equation. Using the fluctuation-dissipation theorem it is possible to do constant-temperature simulations.

The desorption rate constant for an atom is given in variational transition state theory by [6]

$$k = \frac{1}{Z} \int dq \, dp \, e^{-\beta H} \Theta(S) \delta(S),$$

where $Z$ is the partition function for the adsorbed atom, $H$ is the classical Hamiltonian, $\beta = (k_B T)^{-1}$, $\Theta$ is the Heaviside step function, and $\delta$ is the Dirac delta function. The function $S$ separates the region in phase space where the atom is adsorbed ($S < 0$), from the region where it is desorbed ($S > 0$). The integration is over the whole phase space; the star indicates that we have to correct for multiple crossings of the divid-
ing surface \((S = 0)\) \([6]\). Within classical mechanics eq. (1) is exact. The partition function is given by
\[
Z = \int dq \, dp \, e^{-\beta H} \Theta(-S).
\] (2)

It is usual for chemical reactions to choose \(S\) so that the dividing surface in configuration space is near the top of the activations barrier; i.e., the transition state. For desorption this would mean taking \(S = z - z_0\), where \(z\) is the coordinate along the surface normal, and \(z_0\) is a constant indicating the position of the transition state. However, this is not always possible as the top of the barrier for desorption may be at infinity. This leads to a diverging partition function and a vanishing rate constant. Instead we take
\[
S = \frac{p_z^2}{2m} + V_C(z),
\] (3)

where \(m\) is the mass of the adsorbed atom, and \(V_C\) is a potential approximately equal to the substrate–adsorbate potential \([2]\). If \(S > 0\) the adsorbed atom has enough energy to desorb.

At low temperature the Boltzmann factor in eq. (1) far from the surface is small. Hence, it is improbable to find the atom far from the surface, and so simulations will not show any desorptions. As the desorption is an infrequent, but fast, event, we may still be able to evaluate the desorption rate constant from an MD simulation. In order to increase the Boltzmann factor, without raising the temperature, we introduce a compensating Hamiltonian \(U(S)\) via
\[
H = \tilde{H} + U(S),
\] (4)

that contains part of the barrier for desorption. A factor \(\exp(\beta U(0))\) can be taken out of the integration. Doing the simulations with the effective Hamiltonian \(\tilde{H}\) we have a larger Boltzmann factor \(\exp(-\beta \tilde{H})\), so that we can evaluate the desorption rate constant. This way the dynamics changes, however. If we want to know the real dynamics we use the fact that the compensating Hamiltonian is a function of \(S\). Thus the relative probability to find the system at various points on the dividing surface is the same for the real and the effective Hamiltonian. We can therefore start the simulation with \(\tilde{H}\), run the simulation until the atom has enough energy to desorb and is on the dividing surface, and then use that point on the dividing surface as a starting point for a simulations with the real Hamiltonian \([2]\).

3. The effect of corrugation

We have simulated the desorption of Xe from Pd(100). The substrate was represented by a cluster with 12 atoms in the first and 5 atoms in the second layer. We used a harmonic Pd–Pd potential which we fitted to the elastic constants. The Xe–Pd potential was a Lennard-Jones 12–6 potential with bond length 3.194 Å and bond strength 683 K. These values were obtained by fitting to the adsorption energies of Xe on Pd(111), Pd(110), and Pd(100) \([7]\).

We have found reasonable values for the desorption rate constants \([2]\). The activation energy and the pre-exponential factor appear to be temperature dependent. At low temperature the activation energy equals the adsorption energy \(E_{\text{ads}}\) at a 4-fold site. At high temperature it is equal to the adsorption energy averaged over all sites; \(E_{\text{ads}} - 2V\). Here \(2V\) is a measure for the corrugation. The pre-exponential factor is equal to the frequency of the Xe vibration \(\nu_0\) normal to the surface at high temperature. At low temperature it diverges as \(T^{-1}\); the coefficient of \(T^{-1}\) is proportional to \(\nu_0\).

Even more interesting are the results from the dynamics. When the temperature is decreased the probability of finding the Xe atom at the preferred 4-fold site, as expected, increases. Also the probability for desorption from a 4-fold site increases, but much more slowly. This is reasonable as it is easier to desorb from a 2- or 1-fold site.

Fig. 1 shows the kinetic energy of the Xe atom in normal and lateral direction after desorption. The energy is normalized for comparison with a Boltzmann distribution for a temperature equal to the surface's. We note that the distributions of the simulations are not Boltzmann. If we decrease the temperature the desorbed Xe atom becomes relatively colder in lateral and hotter in normal direction. A Boltzmann distribution for
the velocity of the adsorbed Xe atom will be deformed in the collision with the surface that leads to the desorption (see below), and when the Xe atom moves out of the adsorption well due to the conversion of kinetic into potential energy.

The angle $\theta$ of the direction in which the Xe atom desorbs with the surface normal is at high temperature distributed as $\sin \theta \cos \theta$, which corresponds to a scattering from the surface in no preferred direction with a subsequent deformation of the velocity distribution due to the adsorption well. (This desorption-angle distribution is usually called a $\cos \theta$-distribution. We use a slightly different definition.) At lower temperatures the maximum in the distribution shifts to smaller angles (see fig. 2). This effect and the behaviour of the kinetic energy as a function of temperature is related to the corrugation. At high temperature the Xe atom easily diffuses over the surface. It desorbes after a collision with no orientational preference. At low temperature the corrugation leads to barriers for the diffusion. If the Xe atom moves laterally it will collide with these barriers, and be scattered in the direction of the surface normal. A model, called deflection-to-normal model, describing this process gives semi-quantitative agreement with the results of the simulations [2].

4. Coverage dependence

Recent TPD experiments by Siddiqui et al. [8] on Xe desorption from Pt(111) show a peak shift from 93 K at low coverage to 103 K at monolayer coverage ($(\sqrt{3} \times \sqrt{3})$R30° structure). We have used the low-coverage spectra to calibrate the Pt–Xe potential. Existing Xe–Pt potentials give a peak position that is at least 10 K too high [8]. Starting with the Morse potential of Arumainayagam et al. [9] we have scaled the adsorption energy $E_{\text{ads}}$ and the vibration $\nu_0$ of the Xe atom normal to the surface as $E_{\text{ads}} \rightarrow \lambda E_{\text{ads}}$, and $\ln \nu_0 \rightarrow \ln \nu_0 / \lambda$ choosing $\lambda$ to obtain the peak at about 93 K. We have used a temperature increase of 3 K s$^{-1}$ throughout. The result is a Morse potential $V_{\text{Pt–Xe}} = D_e (x - 2)$, where $x = \exp(-\alpha(R_{\text{Pt–Xe}} - R_e))$ with $D_e / k_B = 362.7$ K, $R_e = 3.2$ Å, and $\alpha = 1.227$ Å$^{-1}$. For the Xe–Xe potential we have used a Morse potential fitted to Barker’s X2 potential [10]. The method to compute the desorption rate constant is the same for Xe/Pd(100), except that we have used here two layers of 48 Pt atoms each, and periodic boundary conditions in two dimensions.

The coverage dependence of the TPD spectra depends on the Xe–Xe potential. As the adsorption energy increases with increasing coverage up to a monolayer, the peak is expected to shift, as observed, to higher temperatures. This may be counteracted by an increase in the pre-exponent-
tial factor. We have assumed that the temperature dependence of the activation energy and the pre-exponential factor is negligible. Using just Barker's X2 potential gave a peak somewhat below 131 K. Although the direct interaction between the Xe atoms is dominating, it is clear from literature that for physisorption also substrate-mediated, adsorption-induced dipole, and substrate and adsorbate elastic deformation interactions may be important [11]. Moreover, for Xe charge transfer to the substrate may be important as well [12]. Direct and deformation interactions are automatically included in the simulations. It is apparent, however, from the too high desorption peak that at least some of the other interactions are important as well.

A continuous model predicts that the Xe–Xe dispersion interaction for adsorbed Xe may be as small as 2/3 of the gas-phase value [13]. Making this correction to Barker's X2 dispersion decreases the peak position to somewhat below 121 K. Adding a term that describes the Coulomb repulsion between Xe atoms due to the charge transfer the peak temperature decreases further to 112 K. The magnitude of the charge on Xe can be obtained from the change in the work function due to Xe adsorption [11,14], and the assumption that the charge separation is equal to the normal distance of a Xe atom to the surface. The charge on Xe is then 0.027e. The results of the simulations with the last potential are shown in fig. 3. Polarization of the Xe atoms has only a very small effect.

It is apparent from the foregoing that it is essential to know the influence of the substrate on the Xe–Xe potential. Unfortunately, this influence is not well understood. For example, although the substrate-mediated interaction decrease the dispersion in continuous models, a discrete model predicts a substantial increase [15]. Even less clear are the other interactions caused by the substrate.

5. The effect of steps

We have studied, using the same Xe–Pt potential as for Xe/Pt(111), the influence of steps on the desorption of Xe from Pt(112). Experimentally a peak at low coverage is found at 138 K. The simulations also show a shift to higher temperatures with respect to Pt(111), but it is as much as 16 K to small. Clearly, the steps change the Xe–Pt potential. The attractive interaction for Pt(111) is mostly dispersion interaction. The Smoluchovski effect, however, will lead to a strong electric field at the step, and thus to an interaction with the charge of the Xe atom, and to polarization. We have assumed that the increase of the adsorption energy equals the difference in electrostatic energy of the charged Xe atoms at the step and on the terrace. The charge on Xe is the same as for Xe/Pt(111), and the electrostatic potential difference has been taken from PAX spectra [3]. We have changed the interaction of the Xe atom with the Pt atoms forming the step so that a Xe atom at a step has an increased adsorption energy, whereas the adsorption energy for a Xe atom on a terrace is not changed. This shifts the peak position to 134 K. The TPD spectra show a second peak at 105 K for those atoms desorbing from the terraces when all sites at the steps are occupied. Using the Xe–Xe potential of Xe/Pt(111) we compute this peak at 121 K.

6. Conclusions

The main advantage of MD is that no approximations of the dynamics have to be made. Thus
we have been able to compute desorption rate constants for systems in which the application of other, analytical, theories is questionable. Another advantage is the large amount of details of the desorption obtained. This is very nicely demonstrated for the desorption of Xe from Pd(100).

The weak point of the simulations we have presented is of course the potentials. It is clear however that, as the direct interaction between Xe atoms is well represented, as in the case of Pt(111), the influence of the substrate on the Xe–Xe potential is very important. This influence diminishes the attraction, but is unclear how and exactly how much. Our model of a slight charge transfer seems to work reasonable. Also a reduction of the Xe–Xe dispersion interaction seems to be required. It has also been suggested that polarization of the Xe atom may be important [11]. We have found, however, this effect to be too small. This agrees with pervious studies [12]. Actually, the agreement for Xe/Pt(111) is better than the comparison of the experimental and MD peak positions suggests. A varying temperature increase was used in the experiment. This leads to peaks at somewhat lower temperatures than with our 3 K s−1 increase. For Xe/Pt(112) the manner in which we modified the Xe–Pt potential, and the position of the low temperature peak are unsatisfactory. Both these problems are currently being investigated.

References