

LETTER TO THE EDITOR

Absolute rate of thermal desorption from first-principles simulation

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Abstract

We present a technique for computing by first-principles simulation the absolute desorption rate γ of adsorbate molecules from a surface for any coverage and temperature. The technique is valid when the thermal equilibration rate on the surface is faster than γ , and is based on an exact expression for γ in terms of the difference of non-configurational chemical potentials of gas-phase and adsorbed molecules. This difference is expressed in terms of a potential of mean force, which is computed by constrained first-principles molecular dynamics. The technique is applied to D₂O on the MgO(001) surface at low coverage, using the generalized gradient approximation (GGA) for exchange–correlation energy. Comparisons with experimental temperature programmed desorption data allow an assessment of the accuracy of the GGA for the adsorption of D₂O on MgO(001).

Density functional theory (DFT) is very widely used to model the energetics of surface processes (see e.g. [1, 2]). Nevertheless, its accuracy is known to be rather unreliable. For example, calculated adsorption energies of molecules on surfaces sometimes vary by up to 0.5 eV with different choices of approximation for the DFT exchange–correlation energy. This means that DFT predictions need to be tested in every possible way against experimental data. For adsorption energies, one of the most abundant sources of data is temperature programmed desorption (TPD) experiments (see e.g. [3–6]). However, the problem in fully exploiting such data is that their interpretation requires knowledge of a frequency prefactor, which is often lacking. With the aim of bringing DFT predictions into closer contact with TPD experiments, we show here how to predict absolute desorption rates using dynamical DFT simulations, and we report practical calculations for water adsorbed on MgO(001), which we compare with experimental data. The comparison provides a test of current DFT approximations for the energetics of this system, as well as providing a value for the previously unknown prefactor.

In a TPD experiment, the adsorbate molecules are deposited on a prepared surface. Then, starting from some chosen initial temperature, the temperature is made to increase in a specified way (usually linearly with time), and the desorption rate of the molecules is measured as a function of time. In simple cases, the desorption rate shows a single peak as a function of temperature, but more commonly a number of peaks are observed. The basic formula almost universally used for the analysis of such experiments is the Polanyi–Wigner (PW) equation [6, 7], according to which the rate of change of adsorbate coverage θ (molecules per adsorption site) is given by

$$d\theta/dt = -f\theta^n \exp(-\Delta E/k_B T), \quad (1)$$

where ΔE and n are the activation energy and reaction order for desorption and f is a frequency prefactor. It is assumed in this equation that the desorption rate at any instant depends only on the instantaneous temperature and coverage, and not on the previous history. In general, ΔE and f are expected to depend on coverage θ . In detailed TPD work, experiments are done starting with different initial coverages, and in favourable cases a ‘complete analysis’ is possible [6], in which the coverage dependent activation energy $\Delta E(\theta)$ and prefactor $f(\theta)$ as well as the reaction order can be extracted. However, this is often not possible, and a common practice [8], particularly for first-order desorption, is to use a guessed value for f (a popular default value is 10^{13} s^{-1}) and to deduce ΔE from the temperature of the TPD peak.

These phenomenological procedures for analysing experimental data are very successful on their own terms, but in order to calculate the desorption rate from DFT simulations, we consider it preferable not to assume the PW equation but to start from more fundamental principles and allow PW to emerge from these principles. We shall see that in this way the frequency prefactor can be obtained without any ad hoc assumptions.

In order to explain the first-principles techniques, we need to summarize the statistical mechanics of TPD in a suitably general way. This theory has, of course, been expounded in different forms in many papers and books (see e.g. [4]), but usually in the framework of lattice-gas models, which we specifically wish to avoid here. Following the ideas underlying the PW equation, we assume that the adsorbate–surface system is in thermal equilibrium during the desorption process, so that the desorption rate γ at any instant depends only on temperature and coverage, and not on the previous history. This is equivalent to saying that the thermal equilibration rate is faster than the desorption rate. It is convenient to work with a desorption rate γ defined as the number of desorption events per molecule per unit time ($\gamma = \theta^{-1}d\theta/dt$). Since the surface is always in thermal equilibrium, γ is the same as the desorption rate when the adsorbed gas is in full thermal equilibrium with the gas phase, and can be derived by detailed balance arguments. For adsorbate–gas equilibrium, the chemical potentials μ_{gas} and μ_{ads} of the molecules in the gas phase and on the surface are equal. It is convenient to express these chemical potentials as

$$\begin{aligned} \mu_{\text{gas}}(\rho, T) &= k_B T \ln(\rho \Lambda^3) + \mu_{\text{gas}}^\dagger(T) \\ \mu_{\text{ads}}(\sigma, T) &= k_B T \ln(\sigma \Lambda^2) + \mu_{\text{ads}}^\dagger(\sigma, T), \end{aligned} \quad (2)$$

where ρ and σ are the number densities (per unit volume and unit area, respectively) in the gas and on the surface and $\Lambda = (h^2/2\pi M k_B T)^{1/2}$ is the thermal wavelength (M is the mass of the molecule). Under TPD conditions, ρ is so low that interactions between gas-phase molecules are negligible, so that $\mu_{\text{gas}}^\dagger(T)$ represents only the ro-vibrational part of μ_{gas} , and is independent of ρ . However, μ_{ads}^\dagger includes also interactions between adsorbed molecules, and depends on σ . When $\mu_{\text{gas}} = \mu_{\text{ads}}$, we have

$$\sigma/\rho = \Lambda \exp \left[-\beta \left(\mu_{\text{ads}}^\dagger(\sigma, T) - \mu_{\text{gas}}^\dagger(T) \right) \right]. \quad (3)$$

This equation forms the basis for discussing adsorption isotherms, though that is not our concern here. The desorption rate can now be obtained by considering the rate at which molecules cross a plane drawn parallel to the surface at a distance z_0 large enough to be beyond the range of interaction with the surface, but small compared with the mean free path in the gas. The number of outward crossings per unit area per unit time is $\rho(k_B T/2\pi M)^{1/2}$. However, a fraction $1 - S$ of these crossings represent molecules that arrived from the gas phase, failed to be adsorbed on the surface and returned immediately to the gas phase (S is the sticking coefficient). This ‘detailed balance’ argument shows that the desorption rate per unit area is $\rho S(k_B T/2\pi M)^{1/2}$. From equation (3), the desorption rate per molecule is then

$$\gamma = \frac{S}{\Lambda} \left(\frac{k_B T}{2\pi M} \right)^{1/2} \exp \left[-\beta \left(\mu_{\text{gas}}^\dagger(T) - \mu_{\text{ads}}^\dagger(\sigma, T) \right) \right]. \quad (4)$$

Closely related formulae have been derived by many authors (see e.g. [9, 10]) on the basis of lattice-gas models. However, granted only the basic assumption of surface thermal equilibrium, equation (4) is general and exact, and does not depend on lattice-gas or other approximations.

The first-principles calculation of free energies and chemical potentials of bulk solids and liquids has been extensively investigated over the past 10 years [11–15], but has received comparatively little attention for surface systems. To calculate the difference $\mu_{\text{gas}}^\dagger - \mu_{\text{ads}}^\dagger$, we find it useful to study the number density of adsorbate molecules under conditions of full surface–gas thermal equilibrium as a function of distance z from the surface. We define this to be $\rho y(z)$, with ρ as before the gas-phase density far from the surface, so that $y(z) \rightarrow 1$ as $z \rightarrow \infty$. The number of adsorbed molecules per unit area on the surface is then $\sigma = \rho \int_{-\infty}^{z_0} dz y(z)$, so that from equation (3), the difference of chemical potentials is given by

$$\exp \left[-\beta \left(\mu_{\text{ads}}^\dagger(\sigma, T) - \mu_{\text{gas}}^\dagger(T) \right) \right] = \frac{1}{\Lambda} \int_{-\infty}^{z_0} dz y(z). \quad (5)$$

To obtain a practical computational scheme, we now express $y(z)$ as

$$y(z) = \exp[-\beta\phi(z)], \quad (6)$$

where the quantity $\phi(z)$, i.e. the ‘potential of mean force’ [16], goes to zero as $z \rightarrow \infty$. Basic statistical mechanics [16] then shows that $\phi(z)$ is given by

$$d\phi/dz = -\langle \mathcal{F}_z \rangle_z \quad (7)$$

where the dynamical variable \mathcal{F}_z is the force acting on the molecule along the surface normal (positive outwards), and $\langle \cdot \rangle_z$ indicates the thermal average in the ensemble in which the distance of the molecule from the surface is constrained to be z . This kind of relation between a density such as $y(z)$ and the thermal average of an appropriate force is commonly used in simulation schemes for calculating free energies. The present strategy is therefore to use first-principles molecular dynamics (MD) to calculate $\langle \mathcal{F}_z \rangle_z$ at a series of z values, to integrate this numerically to obtain $\phi(z)$ and hence $y(z)$, and then to perform the z -integral of equation (5) to calculate the difference of chemical potentials and hence the desorption rate. Effectively, our strategy calculates the reversible work performed on transferring a molecule between the gas phase and the surface, and uses the relationship between this reversible work and the difference of non-configurational chemical potentials. We note that the strategy fully includes entropic effects, which are crucial in the frequency prefactor. We also remark that the strategy is valid at any coverage.

To explore the practical application of this strategy, we have studied the case of D₂O adsorbed on the MgO(001) surface at low coverage. (We study D₂O rather than H₂O because we wish to compare with experimental TPD data [17, 18] on D₂O.) There has

already been extensive DFT work on the water/MgO(001) system, some of it employing MD simulation [19–22]. It been deduced from this that water adsorbs in molecular form at low coverage. All the present calculations are done using the VASP code [23], with the projector augmented wave (PAW) technique [24, 25] for solving the Kohn–Sham equation, and the PBE exchange–correlation functional [26]. The simulations use the usual repeated slab geometry, with the lattice parameter set equal to its experimental value $a_0 = 4.23$ Å. Before starting MD, we made extensive static calculations to test the effects of slab thickness and size of surface unit in the periodic cell. Within PBE, the minimum energy for the adsorbed molecule is obtained with the O of D₂O almost above a surface Mg ion, with the plane of the molecule almost parallel to the surface, and with each O–D bond pointing towards a surface O ion when viewed along the surface normal. We find that the static adsorption energy E_{ads} is converged to within ~ 2 meV with respect to slab thickness and within ~ 10 meV with respect to the surface cell for a slab containing three ionic layers, each of which contains $4 \times 4 = 16$ ions in the repeating cell, so that the entire repeating cell contains 48 ions of MgO. The static adsorption energy with PBE is 0.46 eV. (For comparison, with the local density approximation of DFT the same calculations give $E_{\text{ads}} = 0.95$ eV, so this is certainly a case where the adsorption energy depends strongly on the DFT approximation.) In the MD simulations, since these are based on classical statistical mechanics, averages of positional variables are unaffected by atomic masses, and we are free to choose these in any convenient way. Our tests show that good sampling efficiency is obtained with the D mass set equal to 8 amu, the O and Mg masses equal to their physical values and a time step of 1 fs. Our simulations are performed in the (N, V, T) ensemble, using combined Nose and Andersen thermostats [27]. We prevent the slab from wandering during the simulation by fixing the z -component of the position of an atom in the middle layer of the slab.

In order to calculate the mean force $\langle \mathcal{F}_z \rangle_z$, we perform MD simulations with the z -component of the water oxygen position fixed at a chosen value, so that \mathcal{F}_z is the z -force on this atom. The molecule is completely free to translate parallel to the x – y plane, and to rotate and vibrate, with no constraints applied to bond lengths or angles. The duration of the simulation at each z -value is determined by the statistical accuracy required for $\langle \mathcal{F}_z \rangle_z$, and the number of z -values at which simulations need to be done is determined by the accuracy with which we wish to perform the integral of equation (5). We find that a tolerance of better than ± 20 meV on the numerical accuracy of $\mu_{\text{gas}}^\ddagger - \mu_{\text{ads}}^\ddagger$ is achieved with typically 15 z -points and a duration of ~ 40 ps at each. We have performed simulations with these specifications at temperatures of 100, 300, 600 and 800 K, and figures 1 and 2 show results for $\langle \mathcal{F}_z \rangle_z$ and $\phi(z)$ at these temperatures. We note that the form of $\langle \mathcal{F}_z \rangle_z$ changes quite strongly with temperature, having two minima at low temperatures. The reason appears to be that the typical orientations of the molecule depend strongly on z . However, the form of $\phi(z)$ is rather simple at all temperatures, consisting of a single attractive well whose depth decreases markedly with increasing temperature.

To obtain desorption rates γ from equation (4), we need the sticking coefficient S . We have studied this at 300 K by performing a series of 12 simulations, in each of which the molecule is started a distance 6 Å from the surface, given a random thermal velocity and allowed to travel to the surface. In every single case, the molecule sticks to the surface, and there is no evidence for rapid desorption. This indicates that $S = 1$ to a very good approximation. The results for γ are shown on an Arrhenius plot in figure 3. They are well represented by $\gamma = f \exp(-\Delta E/k_B T)$ with $\Delta E = 0.454$ eV and $f = 2.7 \times 10^{15} \text{ s}^{-1}$. We note that the Arrhenius slope ΔE is almost exactly equal to the zero-temperature static adsorption energy $E_{\text{ads}} = 0.46$ eV. In fact, this PW form for γ emerges naturally from equations (4)–(6). At temperatures where TPD is performed, the integral of equation (5) is completely dominated by the region around the minimum of $\phi(z)$.

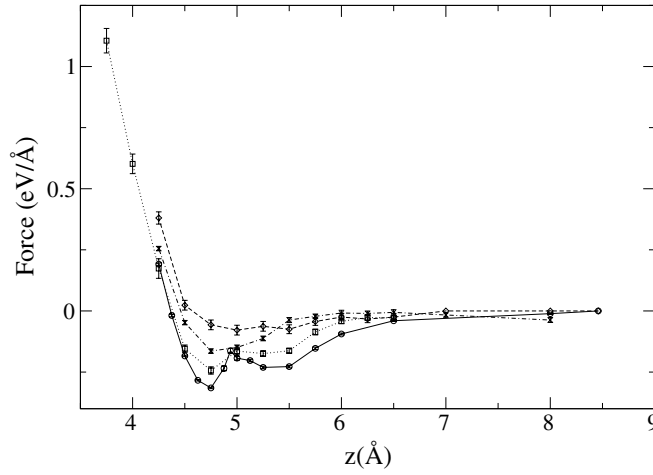


Figure 1. The mean force $\langle \mathcal{F}_z \rangle_z$ on the water O atom as function of the height z of this atom above the surface at temperatures of 100, 300, 600 and 800 K (solid, dotted, chain and dashed curves, respectively, are guides to the eye). Bars on data points show statistical errors. Height z is relative to a fixed atom in the centre of the slab.

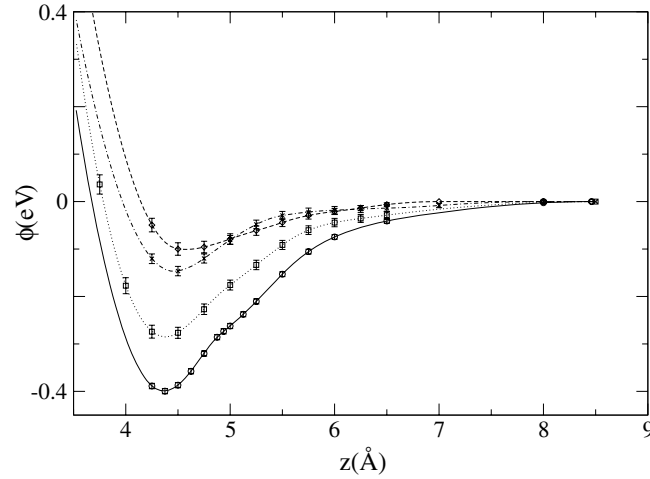


Figure 2. Potential of mean force $\phi(z)$ of the water O atom as function of its height z above the surface at temperatures of 100, 300, 600 and 800 K. Symbols and guides to the eye as in figure 1.

If this minimum occurs at $z = z_{\min}$, we can approximate $\phi(z) \simeq \phi(z_{\min}) + \frac{1}{2}c(z - z_{\min})^2$, perform the integral in equation (5) and obtain

$$\gamma = S \left(\frac{c}{4\pi^2 M} \right)^{1/2} \exp(\beta \phi(z_{\min})). \quad (8)$$

Over the region of interest, $\phi(z_{\min})$ varies approximately linearly with temperature, $\phi(z_{\min}) = -\Delta E - s_0 k_B T$, so that we recover the PW equation for first-order desorption, but now with an explicit formula for the prefactor: $f = S(c/4\pi^2 M)^{1/2} \exp(-s_0)$. We note that $(c/4\pi^2 M)^{1/2}$ is the frequency of oscillation of molecular mass M in the potential well $\phi(z)$. However, for the present system f is greatly enhanced by the entropic factor $\exp(-s_0)$, and this is why f is considerably greater than any physical vibration frequency.

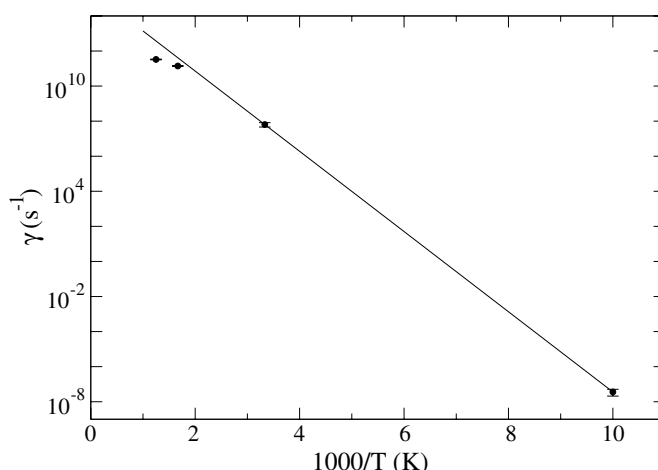


Figure 3. Arrhenius plot of the absolute desorption rate γ of H_2O from $\text{MgO}(001)$ calculated using the PBE exchange–correlation functional. Bars on calculated values show statistical errors; the straight line is drawn to pass through the calculated values at the two lowest temperatures.

It would now be possible to use our temperature-dependent absolute rates to predict the low-coverage TPD spectrum for the $\text{D}_2\text{O}/\text{MgO}(001)$ system. However, it is easy to show that our results seriously overestimate the desorption rate. Experimentally [17, 18], the TPD peak corresponding to sub-monolayer desorption of D_2O occurs at a temperature of 235–260 K. With our activation energy of 0.45 eV and our prefactor of $2.7 \times 10^{15} \text{ s}^{-1}$, our calculated desorption rate at this temperature is $2.6 \times 10^6 \text{ s}^{-1}$, which means that all adsorbed molecules would leave the surface in $\sim 1 \mu\text{s}$. Since the timescale of the experiments is typically over 10 s, it is clear that the simulations overestimate the desorption rate by a factor of $\sim 10^7$.

This large discrepancy gives important information about the (in)accuracy of the GGA exchange–correlation functional for this system. However, before assessing this, we must consider zero-point effects. Our simulations assume classical statistical mechanics for the nuclei. But this is incorrect, because the high vibrational frequencies of the D_2O molecule (80 and 84 THz for symmetric and asymmetric bond stretch, 35 THz for bond bend) imply large zero-point energies. To provide a rough estimate of zero-point corrections, we have performed DFT(PBE) calculations of the vibrational frequencies of the D_2O molecule adsorbed on the surface. These indicate that adsorption lowers the stretch frequencies by 8 and 6 THz, and raises the bond-bending frequency by 1 THz. The corresponding changes of zero-point energies increase the activation energy for desorption by 0.03 eV. However, the calculations also show that there are three high-frequency vibrations of the molecule relative to the surface, having frequencies of 20, 20 and 12 THz, whose zero-point energies decrease the activation energy by 0.10 eV. The conclusion is that the net effect of zero-point corrections is to lower the activation energy of desorption by ~ 0.07 eV, which worsens the discrepancy with experiment.

To complete our assessment of the PBE exchange–correlation functional, we assume provisionally that the frequency prefactor of $2.7 \times 10^{15} \text{ s}^{-1}$ given by our simulations is essentially correct, and that only the activation energy is in error. We then ask what activation energy ΔE would be needed to reproduce the experimental TPD peak temperature of 245 K. We find the result $\Delta E = 0.78$ eV. Since the PBE activation energy is 0.45 eV, we conclude that PBE is too low by ~ 0.3 eV. This is not a surprise, and confirms the inaccuracy of widely used DFT approximations emphasized at the start of this letter.

In conclusion, we have presented a scheme which allows the first-principles calculation of the absolute desorption rate of adsorbed molecules at any temperature and coverage, and we have demonstrated its practical feasibility for the case of D₂O on MgO(001) at low coverage. By ‘feasibility’, we mean that the statistical errors can be reduced enough to allow accurate comparisons with experiment. We believe this scheme will be a useful addition to the toolbox for surface-science modelling. We have shown that it can serve at least two purposes: first, it can provide calculated values of frequency prefactors, which are important in interpreting experimental results. Second, it provides a way of testing particular DFT exchange–correlation functionals against experiment. The need to improve the DFT accuracy of adsorption energetics is widely recognized, and efforts are being made to achieve this (see e.g. [28]). We believe that our scheme will be helpful in testing proposed improvements. We have noted that in its present form the scheme does not include zero-point effects. However, these can be included by using path-integral methods to calculate the potential of mean force, and we are now working on this generalization. We comment that our methods also provide a way of calculating adsorption isotherms by DFT simulation (see equation (3)), though we have not explored this here; this should provide another way of probing the accuracy of DFT.

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