CLASSICAL STOCHASTIC DIFFUSION THEORY FOR DESORPTION FROM SOLID SURFACES

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We present a theory of desorption of atoms and molecules from solid surfaces based on a classical stochastic diffusion formulation. We obtain a simple rate expression which has the form \( R = \left( \frac{\Omega_0}{2\pi} \right) f(T) \exp\left(-\frac{D_0}{kT}\right) \), where \( T \) is the temperature, \( k \) is Boltzmann's constant, \( D_0 \) is the bond enthalpy, and \( \Omega_0 \) is the surface-adsorbate vibrational frequency. For atoms \( f(T) = 1 \), while for molecules \( f(T) \) depends on the parameters for the frustrated rotations at the surface. Application of this theory is reported for the desorption of atoms and molecules. We find that molecules lead to a greatly increased (factor of 100) Arrhenius preexponential factor in excellent agreement with experiment.

1. Introduction

One of the basic processes in surface phenomena is the thermal desorption of adsorbed species from solid surfaces. Due to the development of accurate experimental techniques – such as Molecular Beam Relaxation Spectrometry [1a] (MBRS), Temperature Programmed Desorption [1b] (TPD), Low Energy Electron Diffraction [1c] (LEED), Auger Electron Spectroscopy [1d] (AES), Thermal Desorption Mass Spectrometry [1e] (TDMS), etc. – a vast literature related to adsorption-desorption experiments is available for a large variety of systems. The need for a basic understanding of the nature of such processes and the availability of experimental data have stimulated the proposal of many theoretical methods and models [2–4].

The most commonly used framework for the discussion of desorption is a statistical thermodynamical approach based on transition state theory [2] (TST). Although this method correctly accounts for the observed magnitude of atomic desorption rates, quantitative predictions are difficult since it requires knowledge of the transition state for the desorbing species. This state is not

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well defined, leading to ambiguities in the resulting description of the system. These problems are particularly serious for molecules where various choices of the parameters can lead to several orders of magnitude change in the desorption rates. Although TST does not provide a prediction of specific desorption rates, it does provide a justification for the Arrhenius form,

\[ R = A \exp\left(\frac{-E_d}{kT}\right) \]  

(1.1)

usually used in characterizing experimental desorption rates in the limit of low coverages (no interaction between the adparticles).

A number of authors [3] have combined transition state theory with stochastic trajectory calculations for the evaluation of desorption rates. The theories which employ stochastic trajectory calculations are computationally involved and hence difficult to apply directly to time scales longer than \(10^{-10} - 10^{-11}\) s. This prevents their use for desorption, where time scales of 1 s may be involved.

There are also microscopic theories [4] in which an explicit coupling between the adparticle and the surface phonon modes is introduced to calculate the energy flow between the surface and the adparticle. For reasons that are not fully understood the microscopic approaches lead to discrepancies between experimental and calculated desorption rates for physisorbed atoms. Moreover, there appears to be difficulties in applying these approaches to molecular desorption (no calculations have been reported to date).

The experimental and theoretical studies undertaken over the last two decades have led to a better understanding of the desorption mechanisms. They have, however, simultaneously raised some additional basic questions. One puzzling result pertains to the measurements [1a,5] of both \(A\) and \(E_d\) for the desorption of CO from different metal surfaces. Although the observed values for the preexponential factor (in the limit of low coverage) vary over three orders of magnitude, all of the experimental results indicate that the values of \(A\) are at least two orders of magnitude larger than the corresponding values observed for atomic systems \((A = 10^{13} \text{ s}^{-1})\). In addition, several experiments [5b,5c] lead to different functional relationships between \(A\) and \(E_d\) and the surface coverage.

A puzzling theoretical result is due to Grimmelmann et al. [3] and Adams and Doll [6], who calculated the rate of desorption as a function of surface temperature for Ar and Xe on Pt(111) and He on Xe(111), respectively. These calculations showed the existence of two temperature regimes for desorption in which different values of \(A\) and \(E_d\) were observed. They found that the preexponential factor and the activation energy in the low temperature range are larger than the corresponding values for the high temperature regime. No explanation of this effect was extracted from the theory.

These examples illustrate that the detailed processes governing desorption rates are not yet fully understood. One of the basic reasons for this is that none
of the existing theories yield explicit expressions for the rate of desorption in terms of the microscopic properties (e.g. vibrational frequencies, bond energy, etc.) and dynamics of the adsorbate–surface system. Moreover, with the exception of TST [5a], all of the present theoretical treatments have been applied only to the case of atomic desorption.

In the present paper we develop a theoretical description for desorption [7] which yields a simple rate expression given in terms of the microscopic properties of the system. The rate of desorption is found to have the form

$$R = \frac{\Omega_0}{2\pi} f(T) \exp\left(-\frac{D_e}{kT}\right),$$

where $T$ is the temperature, $k$ is Boltzmann's constant, $D_e$ is the bond enthalpy, and $\Omega_0$ is the surface–adsorbate vibrational frequency. For atoms the factor $f(T) = 1$ but for molecules $f(T)$ depends on the parameters for the frustrated rotations at the surface. For molecules this factor can be $10^2$ to $10^3$, leading to the much larger desorption rates observed for molecules.

In section 2 we derive the rate expression (1.2). This derivation [7] is based on a classical stochastic diffusion theory (CSDT) which follows a procedure proposed by Kramers [8] but modified so as to be appropriate for desorption. In section 3 we describe and discuss the results obtained by CSDT for the desorption of atoms and molecules from solid surfaces. We find that a comparison with available experimental data leads to excellent agreement.

### 2. Theoretical derivation of the rate expression

#### 2.1. Stochastic equation of motion

We shall start by considering the relative motion of the adparticle with respect to the surface atoms. In so doing we shall follow the ideas introduced by Adelman and Doll [9,10]. We consider explicitly the motion of a few surface atoms which are strongly interacting with the adsorbed particle, while the rest of the crystal is assumed to act as a heat bath. Without loss of generality we shall consider the motion of only one surface atom.

We first assume that the adparticle is an atom; a generalization of the results for the case of molecules will be considered in section 2.3. A further simplification is introduced by assuming a one-dimensional system in which both the adatom and the surface atom are restricted to move in a direction normal to the surface. Thus the motion of the adatom will be described by

$$m \ddot{z} = -\frac{\partial V(z - \xi)}{\partial z},$$

where $z$ and $\xi$ are the positions of the adatom and the surface atom, respec-
respectively, \( m \) is the mass of the adatom and \( V(z - \xi) \) is the interaction potential between the adatom and the surface.

The motion of the surface atom will be described by a generalized Langevin equation [9],

\[
m_s \ddot{\xi} = -\frac{\partial V(z - \xi)}{\partial \xi} - m_s \omega_s^2 \xi - m_s \int_0^t \Theta(t - t') \xi(t') \, dt' + \tilde{f}(t),
\]

(2.2)

where \( m_s \) represents the mass of the surface atom; \( \omega_s \) is the characteristic frequency of the solid, \( \Theta(t - t') \) and \( \tilde{f}(t) \) correspond to a memory kernel and random force which include the influence of the heat bath on the motion of the surface atom. These functions, \( \Theta(t) \) and \( \tilde{f}(t) \), are related by the second fluctuation-dissipation theorem [9].

Integrating the memory kernel in eq. (2.2) by parts and taking the Markovian limit [9,11], one obtains a Langevin equation of motion for the surface atom,

\[
m_s \ddot{\xi} = -\frac{\partial V(z - \xi)}{\partial \xi} - m_s \Omega_s^2 \xi - m_s \beta_s \dot{\xi} + f(t),
\]

(2.3)

where \( \Omega_s \) is the effective frequency, \( \beta_s \) is the friction constant, and \( f(t) \) is a random force with a Gaussian distribution [8,9]. The interaction potential, \( V(z - \xi) \), between the adatom and the surface is often described in terms of Morse- or Lennard-Jones-type potentials, leading to nonlinear equations of motion. To avoid this we use parabolic splines to represent \( V(z - \xi) \),

\[
V(z - \xi) = \sum_i V_i(x),
\]

(2.4a)

where \( x = z - \xi \) and

\[
V_i(x) = \begin{cases} 
0, & x < x_i, \\
A_i + B_i x + \frac{1}{2} C_i x^2, & x_i \leq x \leq x_{i+1}, \\
0, & x_{i+1} < x.
\end{cases}
\]

(2.4b)

\( x_i \) and \( x_{i+1} \) being the boundaries of the \( i \)th interval. The fit of eqs. (2.4) is performed in such a way that at any boundary point, \( x_i \), the functions \( V_{i-1} \) and \( V_i \) and their first derivatives are continuous.

We now solve eq. (2.3) formally using Laplace transforms [9] to obtain

\[
\left( p^2 + \beta_s p + \Omega_s^2 \right) \hat{\xi}(p) = (p + \beta_s) \hat{\xi}(0) + \hat{\xi}(0) + \frac{\tilde{f}(p)}{m_s} \\
- \frac{1}{m_s} \int_0^\infty \frac{\partial V(z - \xi)}{\partial \xi} \exp(-pt) \, dt,
\]

(2.5)

where the Laplace transform is denoted by a circumflex.

Consider now the last term of eq. (2.5). Since desorption times are orders of
magnitude larger than the typical vibrational periods the adatom remains close
to its equilibrium position for most of the integration interval \([0, \infty]\). This
means that to a very good approximation we can write (using eq. (2.4))
\[
\int_0^\infty \frac{\partial V(z - \xi)}{\partial \xi} \exp(-pt) \, dt = \sum_i \int_0^\infty \frac{\partial V_i(x)}{\partial x} \exp(-pt) \, dt \approx -\frac{B}{p} - C\tilde{x}(p).
\]
(2.6)
Where we have assumed that the values of \(B_i\) and \(C_i\) remain approximately
constant (at their values \(B\) and \(C\), for the interval containing the equilibrium
value of \(x\)) throughout the range of integration over which the integrand is
appreciably large. Substituting eq. (2.6) into eq. (2.5), solving for \(\tilde{x}(p)\), and
taking the inverse Laplace transform we obtain
\[
\tilde{x}(t) = \frac{B}{m_s} \int_0^t \Xi(t') \, dt' + \frac{C}{m_s} \int_0^t \Xi(t') \, z(t - t') \, dt' + R(t),
\]
(2.7a)
where \(R(t)\) includes the initial conditions and the random force \(f(t)\), and \(\Xi(t)\)
is given by
\[
\Xi(t) = Q^{-1} \{\exp \left[ - (\beta_s - Q) t/2 \right] - \exp \left[ - (\beta_s + Q) t/2 \right] \},
\]
(2.7b)
where \(Q^2 = \beta_s^2 + 4\Omega^2\) and \(\Omega^2 = \Omega_s^2 + C/m_s\).
Substituting eqs. (2.4) and (2.7) into eq. (2.1) and integrating by parts the
convolution term of eq. (2.7a) leads to
\[
mz(t) = - \left[ B_i + C_i z(t) \right] + \frac{C_i}{m_s \Omega^2} \left[ B + Cz(t) \right] - \frac{C_i \Lambda(t)}{m_s} \left[ B + Cz(0) \right]
- \frac{C_i C}{m_s} \int_0^t \dot{z}(t - t') \Lambda(t') \, dt' + C_i R(t),
\]
(2.8a)
where \(B_i\) and \(C_i\) refer to the interval in which \(z(t)\) is being evaluated, \(B\) and \(C\)
refer to the intervals around the equilibrium position, and \(\Lambda(t)\) is given by
\[
\Lambda(t) = \int_t^\infty \Xi(t') \, dt',
\]
(2.8b)
leading to \(\Lambda(0) = 1/\Omega^2\). Eq. (2.8a) is the generalized Langevin equation
describing the motion of the adatom while including the effects of the surface.
For those regions in which the adatom interacts most strongly with the surface
we have \(C_i = C\) and \(B_i = B\), so that eq. (2.8a) can be written as
\[
mz(t) = - \frac{\partial V}{\partial z} \left( 1 - \frac{C}{m_s \Omega^2} \right) - \frac{C^2}{m_s} \int_0^t \Lambda(t') \, \dot{z}(t - t') \, dt' + CR(t),
\]
(2.9)
where \(\partial V(z)/\partial z = B + Cz\). In deriving eq. (2.9) we have used the fact that
\(\Lambda(t)[B + Cz(0)] = 0\) because for \(t\) of the order of desorption times \(\Lambda(t)\) has
decayed to very small values (vide infra). (Note that \(-[B + Cz(0)]\) is the force
around the equilibrium position.)
We now take the Markovian limit of the convolution integral in eqs. (2.8a) and (2.9). This approximation is valid in the present case because the time $t$ appearing in the integral refers to characteristic desorption times. On the other hand, from eqs. (2.7b) and (2.8b) we see that the decay time for $\Lambda(t)$ is $\beta_s^{-1}$. To estimate $\beta_s$ we use the Debye approximation, which gives [9]

$$\beta_s = \frac{1}{6} \pi \omega_D,$$  

where $\omega_D$ is the Debye frequency of the surface. The time $\beta_s^{-1}$ is then of the order of magnitude of the period of a molecular vibration so that $t \gg \beta_s^{-1}$. We can then put $\tilde{z}(t-t') \approx \tilde{z}(t)$ and let $t \to \infty$ in the upper limit of the convolution integral, so that eq. (2.8a) becomes

$$m \ddot{z}(t) = \left[- \left[B_i + C_i \tilde{z}(t)\right] + \frac{C_i}{m_s \Omega^2} \left[B + C \tilde{z}(t)\right] + \frac{C_i \beta_s}{m_s \Omega^2} \tilde{z}(t) + C_i R(t), \right.$$  

and eq. (2.9) can be written as

$$m \ddot{z}(t) = -\frac{\partial V}{\partial z} \left(1 - \frac{C}{m_s \Omega^2}\right) - \frac{C^2 \beta_s}{m_s \Omega^2} \tilde{z}(t) + CR(t).$$

The first term in the right hand side of eq. (2.12) is the product of the force at point $z$, $-\partial V/\partial z$, multiplied by a correction factor, $[1 - (C/m_s \Omega^2)]$. The force $-\partial V/\partial z$ is what would be obtained from theoretical calculations in which the surface atoms are kept fixed. The term $[1 - (C/m_s \Omega^2)]$ represents a correction to the surface-adparticle force (arising through the coupling of the adparticle with the crystal) due to the motion of surface atoms. Thus, the directly calculated surface-adsorbate frequency would be $\omega_0 = \left(C/m_s\right)^{1/2}$, however, the modification due to the motion of the crystal atoms leads to

$$\tilde{\omega}^2 = \omega_0^2 \left(1 - \frac{C}{m_s \Omega^2}\right) = \omega_0^2 \left(\frac{\Omega_s^2}{\Omega_s^2 + \omega_0^2}\right)$$

(a reduced frequency). This may explain why the calculated surface-adsorbate frequencies (i.e. $\omega_0$) are often larger than the experimentally observed values (i.e. $\tilde{\omega}$) [14a].

The limit of $T \to 0$ the correction term becomes unity. This can easily be seen as follows: $\Omega_s$ is given [9] by

$$\Omega_s^2 = \lim_{p \to 0} \left[\hat{\chi}(p)\right]^{-1},$$

where $\hat{\chi}(p)$ is the Laplace transform of the susceptibility, $\chi(t)$, which in the Debye approximation is given by [12]

$$\chi(t) = \int_0^{\omega_n} f(\omega) \rho(\omega) \frac{\sin(\omega t)}{\omega} \, d\omega,$$

where $f(\omega)$ is the Bose–Einstein distribution function and the phonon density
of states is given by $\rho(\omega) = 3\omega^2/\omega_D^3$. Eqs. (2.13) and (2.14) give (in atomic units)

$$\Omega_s^2 = \frac{\omega_D^2}{3} \left( \omega_D - kT \log \left[ \frac{1}{2} + \frac{1}{2} \exp \left( \frac{\omega_D}{kT} \right) \right] \right)^{-1}. \quad (2.15)$$

Thus, $\Omega_s^2 \to \infty$ as $T \to 0$.

Eqs. (2.11) and (2.12) are Langevin-type equations describing the motion of the adatom coupled to the solid surface, which acts as a heat bath. We rewrite them in the form

$$\dot{z} = -B - \Omega_s^2 z - \beta \dot{z} + \left[ CR(t)/m \right]. \quad (2.16)$$

We have thus reduced the equation of motion of the desorbing particle to that of a Brownian particle moving under the influence of the force $-m(\bar{B} + \Omega_s^2 z)$. The parameters $\bar{B}$, $\Omega_s^2$ and $\beta$ of eq. (2.16) are defined in terms of the microscopic quantities appearing in eqs. (2.10) through (1.15). The next step consists in the calculation of the rate of desorption of the adparticles via Kramers' [8] method (modified for desorption). This is done in the next section.

2.2. Rate of desorption for atoms

In a desorption process we are interested in time scales which are much larger than the characteristic time scales of the molecular motion, $\beta^{-1}$ (see eq. (2.16)). Thus, in obtaining an expression for the desorption rate we shall follow the derivation originally suggested by Kramers [8]. We start by considering the generalized Liouville equation,

$$\frac{\partial W}{\partial t} + u \frac{\partial W}{\partial z} + K \frac{\partial W}{\partial u} = \beta u \frac{\partial W}{\partial u} + \beta W + q \frac{\partial^2 W}{\partial u^2}, \quad (2.17)$$

where $W(z, u, t)$ is the probability to find the particle at position $z$ with velocity $u$ at time $t$, and $q = kT\beta/m$. Here $\beta$ is the friction constant in eq. (2.16) and $K$ represents the acceleration caused by the intercation potential, $\bar{V}$, coupling the adatom to the surface. This acceleration, $K$, is given, according to eq. (2.16), by

$$K = - (\bar{B} + \Omega_s^2 z) = - \frac{1}{m} \frac{\partial \bar{V}(z)}{\partial z}. \quad (2.18)$$

Eq. (2.17) is satisfied [8] by the Maxwell–Boltzmann distribution,

$$W_{MB}(z, u) = C_0 \exp \left( - \left[ mu^2 + 2\bar{V}(z) \right]/2kT \right), \quad (2.19)$$

where $C_0$ is a normalization constant. We expect the distribution (2.19) to be valid near the bottom of the potential $\bar{V}$, so that, in the case of desorption, we
will be looking for stationary solution of eq. (2.17) of the form [8]

$$W(z,u) = C_0 \frac{F(z,u)}{z^{3/2}} \exp \left[ - \left( \frac{mu^2 + 2\bar{V}}{2kT} \right) \right], \quad (2.20)$$

where $F(z,u)$ is nearly unity in the neighborhood of $z = 0$ and $F(z,u) \to 0$ for $z \to \infty$. Substitution of eq. (2.20) into (2.17) yields the following equation for $F(z,u)$,

$$u \frac{\partial F}{\partial z} + K \frac{\partial F}{\partial u} = q \frac{\partial^2 F}{\partial u^2} - \beta u \frac{\partial F}{\partial u}. \quad (2.21)$$

This equation can be solved by means of the substitution [8] $\xi = u - az - b$, we can rewrite eq. (2.21) in terms of the variable $\xi$ as

$$-(a - \beta) \xi \frac{\partial F}{\partial \xi} = q \frac{\partial^2 F}{\partial \xi^2}, \quad (2.22)$$

where the parameters $a$ and $b$ are given by

$$a = \frac{1}{2} \left[ \beta + \left( \beta^2 - 4\bar{\Omega}^2 \right)^{1/2} \right], \quad b = - \frac{2\bar{B}}{-\beta + \left( \beta^2 - 4\bar{\Omega}^2 \right)^{1/2}}. \quad (2.23)$$

Integrating eq. (2.22) we obtain

$$F(z,u) = \left( \frac{a - \beta}{2\pi q} \right)^{1/2} \int_0^\xi \exp \left[ - \frac{(a - \beta)\xi^2}{2q} \right] d\xi'. \quad (2.24)$$

In order to obtain an expression for the rate of desorption, we will calculate the flux of desorbing particles at a given distance from the surface, $z_0$. In principle, this distance should be $z_0 = \infty$, that is, $z_0$ should correspond to an atom–surface separation for which the interaction potential, $\bar{V}$, vanishes. If we choose $z_0$ to be some finite distance, the flux we should calculate must take into account only those particles which have sufficient kinetic energy to escape. Thus, the desired flux at a given value of $z_0$ is

$$j(z_0, u_0) = \int_{u_0}^{\infty} W(z_0, u) u \, du, \quad (2.25)$$

where $u_0$ is the smallest (positive) velocity for which a particle at $z_0$ will desorb, i.e.

$$D_e = \bar{V}(z_0) + \frac{1}{2}mu^2. \quad (2.25)$$

Substitution of eqs. (2.20) and (2.23) into (2.24) gives

$$j(z_0, u_0) = C_0 \left( \frac{a - \beta}{2\pi q} \right)^{1/2} \exp \left( - \frac{\bar{V}(z_0)}{kT} \right) \times \int_{u_0}^{\infty} \exp \left( - \frac{mu^2}{2kT} \right) \int_0^\xi \exp \left( - \frac{(a - \beta)\xi^2}{2q} \right) d\xi'' u \, du. \quad (2.26)$$
Integrating by parts and rearranging we obtain
\[ j(z_0, u_0) = C_0 \frac{kT}{m} \exp \left( - \frac{[mu_0^2 + 2\tilde{V}(x_0)]}{2kT} \right) \mathcal{T}(T), \] (2.27a)
where
\[ \mathcal{T}(T) = \phi(\alpha_1) + \exp(-\eta) \left( \frac{\eta \beta kT}{2ma} \right)^{1/2} [1 - \phi(\alpha_2)], \] (2.27b)
with
\[ \alpha_1 = \left( \frac{m(a - \beta)}{2kT\beta} \right)^{1/2} \left[ u_0 - (az_0 + b) \right], \quad \alpha_2 = \left( \frac{ma}{2kT\beta} \right)^{1/2} \left[ -\theta(az_0 + b) + u_0 \right], \]
\[ \theta = 1 - \beta/a, \quad \eta = \theta \beta (az_0 + b)^2 / 2q. \]

The symbol \( \phi(\alpha) \) stands for the error function [13]. Substituting eq. (2.25) into (2.27) leads to the final expression for the flux,
\[ j(z_0, u_0) = C_0 \frac{kT}{m} \mathcal{T}(T) \exp \left( - \frac{D_c}{kT} \right). \] (2.28)

The rate for a desorption process is given [8] by the ratio of the flux (eq. 2.24) at \( z_0 \) to the number of particles, \( N_0 \), at the surface. As discussed above, the distribution function of the particles in the neighborhood of the equilibrium distance, \( R_e \), is given by \( W_{MB} \), eq. (2.19). Thus, the number of particles, \( N_0 \), is obtained by
\[ N_0 = C_0 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp \left( - \frac{mu^2}{2kT} - \frac{\tilde{V}(z)}{kT} \right) \, dz \, du \]
\[ = C_0 \left( \frac{2\pi kT}{m} \right)^{1/2} \int_{-\infty}^{\infty} \exp \left( - \frac{\tilde{V}(z)}{kT} \right) \, dz, \] (2.29)
where the limits in the integral over \( z \) have been taken from \(-\infty \) to \( \infty \) because the integrand becomes negligibly small for values of \( z \) far away from \( z = 0 \).

For experimentally interesting temperature ranges (where \( kT \ll D_c \)), one can approximate the interaction potential, \( \tilde{V}(z) \), by a harmonic potential to obtain
\[ N_0 = C_0 (2\pi kT/m\Omega_0), \] (2.30)
where \( \Omega_0 \) is the value of \( \tilde{U} \) (cf. eq. (2.16)) at the bottom of the potential well. The validity of this approximation will be discussed in more detail in the next section.

Combining eqs. (2.28) and (2.29) leads to a desorption rate of the form
\[ R = \frac{j}{N_0} = \left( \frac{kT}{2\pi m} \right)^{1/2} \mathcal{T}(T) \left[ \int_{-\infty}^{\infty} \exp \left( - \frac{\tilde{V}(z)}{kT} \right) \, dz \right]^{-1} \exp \left( - \frac{D_c}{kT} \right), \] (2.31a)
and using eq. (2.30) for $N_0$ leads to

$$R = \frac{Q_0}{2\pi} T(T) \exp\left( -\frac{D_e}{kT} \right),$$

(2.31b)

as the final expression for the desorption rate of atoms from solid surfaces. A similar expression (but without the $T(T)$ term) has previously been derived from TST by Garrison and Adelman [17].

2.3. Rate of desorption for molecules

Next, we consider the case of a molecule desorbing from a solid surface. For such a system, in addition to the translational motion, there also exist frustrated motions, such as, frustrated rotations and translations. For example, considering the diatomic molecule CO, the most important frustrated motion corresponds to the bending mode of the oxygen atom about the surface–carbon bond. For the free molecule there is no direct coupling between the pure translational and the pure rotational motions, hence the coupling between the two motions is through the surface. Thus, the total interaction potential between the molecule and the solid surface can be written in the form

$$V_{\text{total}} = \tilde{V}(z) + V_{\text{rot}}(\gamma),$$

(2.32)

where $\tilde{V}(z)$ and $V_{\text{rot}}(\gamma)$ represent the potentials due to pure translation and frustrated rotation (i.e. the bending mode), respectively. In such a case, the molecules, which are in equilibrium with the surface, will have a Maxwell–Boltzmann distribution of frustrated rotational energy. The total distribution function, obtained as a solution to the generalized Liouville equation, will have the form

$$W(z,u,\gamma,\dot{\gamma}) = W(z,u) \exp\left( -\frac{\mu l^2 \Omega_r^2 \gamma^2 + \mu l^2 \dot{\gamma}^2}{2kT} \right),$$

(2.33)

where $W(z,u)$ is defined in eq. (2.20) and the harmonic approximation is used for the frustrated rotational motions [14] (here $\mu$ is the reduced mass for the frustrated rotational motion, $l$ the corresponding length and $\Omega_r$ is the rotational frequency).

Due to the coupling of the translational and rotational motions to the surface, we assume that the energy stored in the frustrated rotation can be converted to translational kinetic energy of the desorbing molecule. As a result we have to modify eq. (2.25) as follows

$$D_e = \tilde{V}(z_0) + \frac{1}{2} \mu u_0^2 + \frac{1}{2} \mu l^2 \dot{\gamma}^2 + \frac{1}{2} \mu l^2 \Omega_r^2 \gamma^2.$$  

(2.34)

Substituting the distribution function (2.33) and eq. (2.34) into (2.24) and averaging over the rotational motion, we obtain

$$j(z_0, u_0) = C_0 \frac{kT}{m} \exp\left( -\frac{D_e}{kT} \right) T(T) \int_{-\gamma_0}^{\gamma_0} \int_{-\dot{\gamma}_0}^{\dot{\gamma}_0} d\gamma d\dot{\gamma},$$

(2.35)
where $\gamma_0$ is the maximum bending angle for the molecule and $\dot{\gamma}_0$ the corresponding maximum angular velocity.

Similarly, the number of particles at the bottom of the interaction potential, $V_{\text{total}}$, is given by

$$N_0 = C_0 \left( \frac{2\pi kT}{m} \right)^{1/2} \left[ \frac{2\pi kT}{\mu l^2 \Omega_r} \right] \phi \left[ \left( \frac{2kT}{\mu l^2 \Omega_r^2} \right)^{1/2} \right] \int_{-\infty}^{\infty} \exp \left( -\frac{\tilde{V}(z)}{kT} \right) \, dz,$$

\hspace{1cm} (2.36a)

or, in the case of a harmonic potential (see eq. (2.30)), by

$$N_0 = C_0 \left( \frac{2\pi kT}{m\Omega_0} \right) \left( \frac{2\pi kT}{\mu l^2 \Omega_r} \right) \phi \left[ \left( \frac{2kT}{\mu l^2 \Omega_r^2} \right)^{1/2} \right] \int_{-\infty}^{\infty} \exp \left( -\frac{\tilde{V}(z)}{kT} \right) \, dz.$$

\hspace{1cm} (2.36b)

(recall that $\phi(\alpha)$ denotes the error function). For typical values (see figs. 1 and 3) of the parameters $T, \mu, l$ and $\Omega_r$, the error function in eq. (2.36) is practically unity. As a result the general expression for the desorption rate of molecules adsorbed on solid surfaces is

$$R = \left( \frac{kT}{2\pi m} \right)^{1/2} \left( \frac{2\mu l^2 \Omega_r^2\gamma_0^2}{\pi kT} \right) T(T) \left[ \int_{-\infty}^{\infty} \exp \left( -\frac{\tilde{V}(z)}{kT} \right) \, dz \right]^{-1} \exp \left( -\frac{D_e}{kT} \right),$$

\hspace{1cm} (2.37a)

and approximating $\tilde{V}$ by a harmonic potential we obtain

$$R = \frac{\Omega_0}{2\pi} \left( \frac{2\mu l^2 \Omega_r^2\gamma_0^2}{\pi kT} \right) T(T) \exp \left( -\frac{D_e}{kT} \right).$$

\hspace{1cm} (2.37b)

As a last step of the derivation we shall consider the temperature dependence of the function $T(T)$, eq. (2.27b). A close examination of this function shows that for most physical systems, including both physisorption and chemisorption of atoms and molecules, the parameters in the right-hand side of eq. (2.27b) are such that $T(T)$ is equal to unity (independent of the choice of $z_0$). In particular, for systems such as Xe and K on W(111) and CO on Ni(110), this function is unity to one part in $10^6$ up to $T \approx 10^6 \text{ K}$. Thus, we can take $T(T) = 1$ in eqs. (2.31) and (2.37) leading to

$$R_{\text{atom}} = \frac{\Omega_0}{2\pi} \exp \left( -\frac{D_e}{kT} \right),$$

\hspace{1cm} (2.38a)

$$R_{\text{molecule}} = \frac{\Omega_0}{2\pi} \left( \frac{2\mu l^2 \Omega_r^2\gamma_0^2}{\pi kT} \right) \exp \left( -\frac{D_e}{kT} \right).$$

\hspace{1cm} (2.38b)
3. Results and discussion

We shall now consider some examples of the application of the theory presented in the previous section. In the case of atomic desorption we shall compare theoretical and experimental results for both chemisorption and physisorption (the two limits of strong and weak interaction potentials). We

![Graph](a) Desorption rates for a chemisorbed atomic system K on W(111) (b) Desorption rates for a physisorbed atomic system Xe on W(111). The values of $D_e$ and $\Omega_0$ used in eq. (2.31a) are the experimentally derived values quoted by De et al. [4a].
shall also discuss the temperature dependence of the desorption rate and the situations in which deviations from Arrhenius behavior would be expected.

3.1. Atomic desorption

The adsorption (and hence desorption) of atoms onto solid surfaces is conventionally partitioned into the weakly bound adsorbed (physisorption) and the strongly bound adsorbates (chemisorption) with the dividing line chosen as ~ 10 kcal/mol, so that only chemisorbed particles remain bound at room temperature. As an example of chemisorption we studied the system K on W(111) (bond energy 2.64 eV), while as a prototype physisorbed system we considered Xe on W(111) (bond energy 0.22 eV). These two systems have been previously studied both experimentally [15] and theoretically [3c,4a].

In fig. 1a we compare the calculated (using eq. (2.31 b)) and experimental [15] rates of desorption as a function of temperature for chemisorbed K on W(111). In addition, the results calculated by De et al. [4a] are shown. In these calculations we used the surface–adsorbate potential, \( V(z) \), obtained from the same parameters of ref. [4a]. For this system our results deviate from experiment by ~ 0.2 orders of magnitude, well within the experimental uncertainty.

The results for the desorption of physisorbed Xe from W(111) are plotted in fig. 1b with a comparison both to the experimental data [15c] and to the theoretical results of De et al. [4a] (the same parameters were used in both calculations). Again we find that the desorption rate obtained from eq. (2.31b) is in excellent agreement with experiment. In this case (physisorption) the results of De et al. show a discrepancy of ~ 2 orders of magnitude from the experimental data. This discrepancy may be related to the fact that De et al. use a substrate–adsorbate potential which includes only linear coupling to the substrate phonon spectra (eq. (2.26a) of ref. [4a]). In addition, they only consider single quantum transitions in the vibrational ladder for the calculation of the first passage time. Both of these assumptions might not be adequate for the treatment of physisorbed systems (where the anharmonicity is large).

These results clearly show that eq. (2.31b) provides a very accurate description of the rate of desorption of atoms from solid surfaces. The simple relation between the rate of desorption, \( R \), and the characteristic microscopic parameters of the system, \( \Omega_0 \) and \( D_e \), makes it possible to predict one of the quantities from experimental determinations of the other two. In general, the experimental determination of frequencies is more accurate than that of absolute rates of desorption; thus, eq. (2.31b) could be used as an important tool to accurately predict desorption rates.

As discussed in the previous section, eq. (2.31b) was obtained from eq. (2.31a) by assuming that the potential \( \tilde{V}(z) \) could be approximated by a harmonic potential with frequency \( \Omega_0 \). This assumption is justifiable whenever \( kT \ll D_e \). This turns out to be the case in the range of temperatures covered by
the experimental results shown in figs. 1a and 1b. However, when this condition is not fulfilled the rate of desorption should be calculated using eq. (2.31a). In such a case the potential $V(z)$ can no longer be approximated by a harmonic potential (with $kT$ comparable to $D_e$ one must obviously include the anharmonic terms implicit in the Morse function) and the preexponential factor becomes temperature dependent. This is a consequence of the fact that
the probability of finding a particle at a point \( z \) near the surface is no longer symmetric about the equilibrium position, \( z = 0 \). As a result, for high temperatures, the desorption rate does not follow the simple Arrhenius form. This is shown for K on W(111) in fig. 2a and for Xe on W(111) in fig. 2b. Here we see that for very high temperatures (outside the experimentally accessible range) the rate of desorption could be interpreted in terms of an Arrhenius-like expression with smaller values for both \( D_e \) and \( \Omega_0 \). This behavior has been previously found theoretically by Tully and coworkers [3b,16] and by Adams and Doll [6]. However, from their dynamical calculations, it was not possible to determine the origin of this effect.

3.2. Molecular desorption

Several molecular desorption systems have been studied experimentally [1a,5,18]. A common characteristic feature is the large preexponential factor, several orders of magnitude above the \( A = 10^{13} \) expected for atomic desorption.

As an example of molecular desorption we have considered CO chemisorbed on Ni(110). In fig. 3 we present the results of our calculations (eq. (2.37b)) as well as the experimental values of Helms and Madix [1a]. We also show the rate of desorption that one would obtain if the CO were treated as an atom (eq. (2.31b)). (The parameters needed to evaluate eq. (2.37b) were taken from refs. [1a] and [12] and are shown in fig. 3.) The limits of integration in eq.
(2.35) for this system were taken to be \( \gamma_0 = \pi/2 \) and \( \dot{\gamma}_0 = \Omega_r \gamma_0 \). The excellent agreement between the theoretical calculation and the experimental data shown in fig. 3. suggests that the frustrated rotational motion is responsible for the two orders of magnitude increase in the preexponential factor. As in the case of atomic desorption, the use of the more general expression (2.37a) will lead, for experimentally accessible temperature ranges, to the same results as eq. (2.37b). However, for very high temperatures the current expression, eq. (2.37a), will lead to a non-Arrhenius rate just as in the atomic case (vide supra).

A close examination of fig. 3 shows that the difference between the theoretical and experimental rates is not uniform. This behavior is due to the explicit temperature dependence of the preexponential factor in eq. (2.37). In fig. 4 we plot the preexponential factors in eqs. (2.31a) and (2.37a) using the parameters shown in fig. 3. It is clear that the atomic case the temperature dependence of \( A \) is important only for extremely high temperatures \( (T > 2000 \text{ K}) \), while in the molecular case the temperature dependence of \( A \) is important at all temperatures. Unfortunately, over the small range of temperatures commonly accessible to experiment, the observed rates can be fitted by an Arrhenius form (1.1) in which the temperature dependence in \( A \) is combined into the \( E_d \) term.
3.3 Comparison with transition state theory (TST)

The most commonly used formula for the rate of desorption from solid surface is the TST expression:

\[ R_{\text{TST}} = \frac{kT}{h} \left( \frac{f^*}{f_{\text{ad}}} \right) \exp \left( \frac{-E_d}{kT} \right), \]  

(3.1)

where \( E_d \) is the activation energy, \( f^* \) and \( f_{\text{ad}} \) are the partition functions for the transition state and the adsorbate layer, respectively, and \( h \) is Planck's constant.

For atomic desorption the ratio \( f^*/f_{\text{ad}} \) can be evaluated (Garrison and Adelman [17]) by assuming that the transition state corresponds to an adsorbate infinitely separated from the surface leading to a preexponential factor equal to \( \Omega_0/2\pi \). This corresponds exactly to our result (2.31b) except for the factor \( Y(T) \) (which is here unity for the normal gas/surface interface).

The very large preexponential factors observed for molecular desorption \( (A \approx 10^{15}) \) could not be explained by using the procedure outlined by Garrison and Adelman [17]. As a consequence attempts were made to estimate the ratio of the partition functions. For example, Pfünür et al. [5a] assumed that at the transition state the desorbing molecule is rotating freely and that is immobile at the surface. Their final form for the preexponential factor is given by

\[ A = \frac{2\pi m (kT)^2}{h^3} \frac{1}{N_s - N f_{\text{rot}}(\text{CO})}, \]  

(3.2)

where \( N_s \) is the total number of sites on the surface, \( N \) is the number of occupied sites, and \( f_{\text{rot}}(\text{CO}) \) is the rotational partition function of CO under desorption conditions. For \( T = 450 \text{ K} \) their estimate of the preexponential factor is \( A \approx 1.2 \times 10^{18} \text{ s}^{-1} \) while the value obtained from eq. (2.37b) is \( 2.3 \times 10^{15} \text{ s}^{-1} \). As Pfünür et al. indicate [5a] their estimate is too high by \( -2 \) orders of magnitude. A comparison of eqs. (3.2) and (2.37b) shows that the present theory (CSDT) leads to a quite different temperature dependence of the preexponential factor compared to eq. (3.2).

4. Conclusions

We have presented a theoretical model for the desorption of atoms and molecules from solid surfaces leading to a simple expression for the rate of desorption (eqs. (2.38)) involving only microscopic parameters (vibrational frequencies and bond energies) of the adsorbed system that are accessible to experimental determination. The theoretical results are in excellent agreement with the experimental data. Since the theoretical rate involves only parameters that can be independent determined from experiment and theory this method
can be used as a powerful tool for the accurate prediction of desorption rates for a variety of atomic and molecular systems. The theory presented herein is constrained to the limit of low coverages; its extension to higher coverages will be presented elsewhere [18].

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