Non-Markoffian Theory of Activated Rate Processes II. Thermal Desorption

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(*Received 17 August 1982*)

Abstract. A model for thermal desorption, described by a one dimensional classical generalized Langevin equation (GLE) for the motion of an adatom, is solved by reducing the GLE to a Fokker Planck equation in action space. The escape rate is obtained as the inverse mean first passage time for the particle to achieve a threshold energy (or action). A calculation using parameters corresponding to the desorption of Ar from W is compared with quantum mechanical results for the same model.

1. INTRODUCTION

Thermal desorption is an extensively studied phenomenon in surface chemistry.[1] Theoretical descriptions of this process have been usually based on one of the following approaches: (a) The Kramers' theory of activated rate processes is used to derive a rate for a one dimensional model (Fig. 1) of the desorption process[2] (limiting forms of the Kramers' result like the transition state theory (TST) have also been used[3]). (b) The quantum levels of the adsorbed particle in its (averaged) potential well are calculated, the quantum mechanical transition probabilities between these levels are evaluated and a master equation is set using these transition rates. The one dimensional model of Fig. 1 and the golden rule expression for the rate are usually used, and dephasing is assumed to be fast in the timescale considered.[4-6] In addition, simulations based on stochastic classical trajectories (SCT) have been quite useful in studying the dynamics of "real" 3-dimensional desorption models.[7]

The Kramers' theory starts from the Langevin equation for a particle in a potential well $V(x)$:

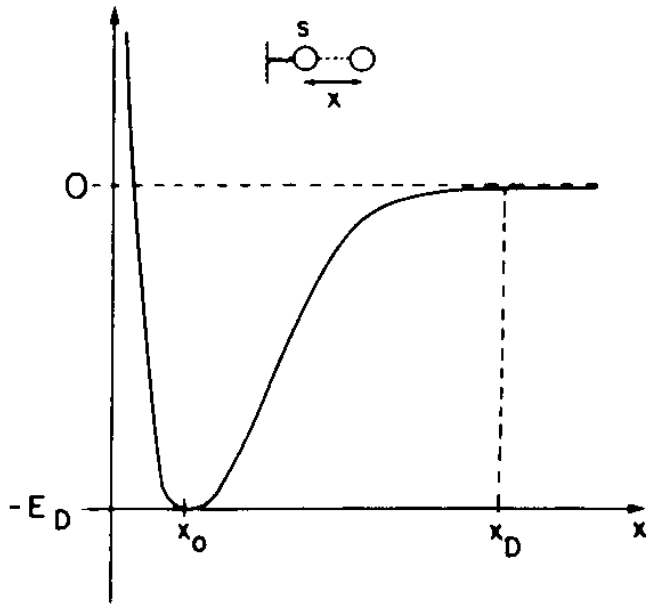

Fig. 1. Pictorial representation of a one-dimensional model of an adatom bound to a surface atom: $x = X - Y$ where X designates the adatom position and Y is the coordinate of the surface atom.

$$\ddot{x} + \frac{1}{M} dV(x)/dx + \gamma\dot{x} = \frac{1}{M} R(t) \qquad (1)$$

where M is the mass of the particle, γ is the damping rate and R is a stationary Gaussian random force satisfying

$$\langle R(t)\rangle = 0; \quad \langle R(0)R(t)\rangle = 2\gamma MkT\delta(t). \qquad (2)$$

The theory results in different expressions for the rate, depending on the strength of the coupling to the heat bath, represented by γ. All these expressions contain the factor $\exp(-E_D/kT)$ and differ in the pre-exponential coefficient: in the low and high friction limits the rate is linear and inversely proportional to γ, respectively. Intermediate cases result in a more complicated γ dependence. The case where γ is low enough so that all particles which reach a certain critical position escape from the well, but high enough to maintain a Boltzmann equilibrium in the well region and a unit sticking probability, is described by the transition state theory (TST), with a γ independent escape rate.

It should be noticed that energy master equations, with transition rates proportional to the strength of coupling to the heat bath, correspond to Kramers' low friction limit. Kramers' theory in this case yields a diffusion equation for the energy, which is the analog of the energy master equation mentioned above. Furthermore, the escape criterion is similar: a particle is considered to have escaped the well if its energy becomes positive (see Fig. 1). The main point of difference between the two approaches lies in the assumption, inherent in Eqs. (1) and (2), that the timescale associated with the thermal bath (i.e the substrate) is much shorter than that which characterizes the adatom. In many situations (chemisorption or strong physisorption) the opposite is true and in many others the two timescales are comparable.* The energy master equation with the quantum mechanically calculated transition rates can easily handle this situation as long as the level widths associated with the transition rates are small relative to the level spacing. Kramers' theory, on the other hand, requires modification: Eq. (1)

* The timescale for the adatom motion is determined by the well frequency and that of the substrate by the surface Debye frequency.

should be replaced by the generalized Langevin equation (GLE)

$$\ddot{x} + M^{-1}dV(x)/dx + \int_0^t d\tau Z(t-\tau)\dot{x}(\tau) = M^{-1}R(t) \quad (3)$$

$$\langle R(t)\rangle = 0; \quad \langle R(0)R(t)\rangle = MkTZ(t) \quad (4)$$

$$\int_0^\infty Z(t)dt = \gamma \quad (5)$$

where $Z(t)$ is characterized by a finite relaxation time τ_c.

The required modification of the Kramers' theory in the low friction limit involves a reduction of Eqs. (3)–(4) to a diffusion equation for the energy, or for the action variable of the particle. Such a reduction is possible if the inequalities

$$\gamma \ll 1/\tau_c \ll \omega \quad (6)$$

(ω being the frequency of motion in the well) are satisfied. The result is[8-10]

$$\frac{\partial P(J,t)}{\partial t} = \frac{\partial}{\partial J}\left[\mathscr{E}(J)\left(kT\frac{\partial}{\partial J} + \omega(J)\right)P(J,t)\right] \quad (7)$$

where J is the action variable (related to the energy through $E(J) = \int^J \omega(J)dJ$) and where

$$\mathscr{E}(J) = 2M\sum_{n=1}^{\infty} n^2 |x_n|^2 \hat{Z}_n^c. \quad (8)$$

In Eq. (8) $\hat{Z}_n^c$ is given by

$$\hat{Z}_n^c = \hat{Z}_n^c(\omega(J)) = \int_0^\infty dt \cos(n\omega(J)t)Z(t) \quad (9)$$

and x_n are the coefficients of the expansion of the *deterministic* motion

$$x(t) = \sum_n x_n(J)\exp(\mathrm{i}n\phi(t)) \quad (10)$$

where ϕ is the angle variable of the particle.

These results are still not suitable to describe a desorption process, because the coupling to the heat bath was taken to be position-independent. In fact, since during the desorption the atom detaches itself from the heat bath, both γ (or Z) and R become position-dependent (and should vanish for large x). In the present paper we apply our approach to the non-Markoffian theory of activated rate processes[9] to a one dimensional model for desorption of an atom from a surface. The model (see insert to Fig. 1) has been used by several authors in a similar context, most recently by Efrima et al.[6] who have used this model to derive an energy master equation. We use our method to explore the effect of the non-Markoffian behavior on the desorption rate, to discuss the use of classical vs. quantum mechanics for the problem and to study the effects of unharmonicity and of multiphonon transitions.

II. MODEL AND MATHEMATICAL DEVELOPMENT

To represent better the physics of a desorption process we replace Eq. (3) by

$$\ddot{X} = -M^{-1}\partial V(X-Y)/\partial X \quad (11)$$

$$\ddot{Y} = -M_s^{-1}\partial V(X-Y)/\partial Y - \omega_s^2 Y - \int_0^t d\tau Z(t-\tau)\dot{Y}(\tau) + M_s^{-1}R(t) \quad (12)$$

X is the coordinate of the adatom of mass M, and Y that of the surface atom of mass M_s. The latter is characterized by a frequency ω_s and is subjected to random force and damping (satisfying Eq. (4)) which arise from its coupling to the rest of the lattice. The origin of coordinates is taken to be the equilibrium position of the surface atom in the absence of the adatom.

We introduce a transformation to the center of mass and relative coordinates by defining

$$x = X - Y$$
$$y = (MX + M_sY)/(M + M_s) \quad (13)$$
$$\mu = MM_s/(M + M_s).$$

Inserting (13) into (11)–(12) we obtain

$$\ddot{x} = -\mu^{-1}\partial V(x)/\partial x + \omega_s^2\left(y - \frac{\mu}{M_s}x\right) + \int_0^t d\tau Z(t-\tau)\left[\dot{y}(\tau) - \frac{\mu}{M_s}\dot{x}(\tau)\right] - M_s^{-1}R(t) \quad (14)$$

$$\ddot{y} = -\frac{\mu}{M}\omega_s^2\left(y - \frac{\mu}{M_s}x\right) - \frac{\mu}{M}\int_0^t d\tau Z(t-\tau)\left[\dot{y}(\tau) - \frac{\mu}{M_s}\dot{x}(\tau)\right] + (\mu/MM_s)R(t). \quad (15)$$

We note that the transformation (13) is a major departure from an earlier treatment of the same model: Efrima et al.[6] have rewritten Eq. (11) as

$$\ddot{X} = -M^{-1}(\partial/\partial X)\langle V\rangle_Y - M^{-1}(\partial/\partial X)(V - \langle V\rangle_Y) \quad (16)$$

where $\langle V\rangle_Y = \langle V(X-Y)\rangle$ is a thermal average over the position of the surface atom, and where the second term in the r.h.s. of (16) provides a perturbation which induces transitions between the levels associated with $\langle V\rangle_Y$. The energy criterion for desorption is then related to a threshold energy defined for the adatom moving in a potential $\langle V\rangle_Y$. We use the energy criterion with a threshold associated with the energy of the relative (adatom–surface atom) motion. As we shall see, this is not just a semantic difference and it leads to different physical conclusions.

To proceed, we formally solve Eq. (15) and substitute the resulting expressions for $y(t)$ and $\dot{y}(\tau)$ in Eq. (14). The result is

$$\dot{v} = -\mu^{-1}\frac{\partial}{\partial x}V(x) - \int_0^t d\tau z(t-\tau)v(\tau) + \mu^{-1}\rho(t) \quad (17)$$

where

$$z(t) = \frac{\mu}{M_s}\left[Z(t) - \frac{\mu}{M}\int_0^t d\tau B(t-\tau) \times \int_0^\tau d\tau' Z(\tau-\tau')Z(\tau') + \omega_s^2 B(t) - \frac{\mu}{M}\omega_s^2\int_0^t d\tau B(t-\tau)\int_0^\tau d\tau' Z(\tau')\right] \quad (18)$$

$$\rho(t) = \mu\left[u(0)\int_0^t d\tau B(t-\tau)Z(\tau) + \omega_s^2\left(y(0) - \frac{\mu}{M_s}x(0)\right)B(t) - \frac{1}{M_s}R(t) + \frac{1}{M+M_s}\int_0^t d\tau\left(R(\tau)\int_0^{t-\tau} d\tau' B(t-\tau-\tau')Z(\tau') + \omega_s^2 B(t-\tau)\int_0^\tau d\tau' R(\tau')\right)\right] \quad (19)$$

(the argument (0) denotes evaluation at $t = 0$) and where

$$v = \dot{x}; \qquad u = \dot{y}. \tag{20}$$

The function $B(t)$ is defined from

$$\int_0^\infty dt \exp(-st)B(t) \equiv \hat{B}(s) = s\Big/\left(s^2 + \frac{\mu}{M}s\hat{Z}(s) + \frac{\mu}{M}\omega_s^2\right) \tag{21}$$

with

$$\hat{Z}(s) = \int_0^\infty \exp(-st)Z(t)dt.$$

Note that $B(t=0) = 1$ if $\hat{Z}(s)$ is zero or finite for $s \to \infty$. Using this and Eq. (19) we can show that

$$\langle \rho \rangle = 0 \tag{22}$$

$$\langle \rho(0)\rho(t)\rangle = \mu k T z(t). \tag{23}$$

To obtain Eq. (23) we also have to assume

$$\left\langle y(0) - \frac{\mu}{M_s}x(0)\right\rangle = \langle Y(0)\rangle = 0 \tag{24}$$

$$\langle u(0)Y(0)\rangle = 0 \tag{25}$$

$$\langle (Y(0))^2\rangle = kT/(M\omega_s^2). \tag{26}$$

Equation (23) constitutes the fluctuation dissipation theorem for the motion associated with the relative coordinate x. Note that the need to make the assumptions (24)–(26) about the initial values $u(0)$ and $Y(0)$ arises from the fact that any particular initial values give rise to transient non-stationary contributions to $\rho(t)$. Only an initial thermal distribution for the surface atom results in the required properties for ρ and z with ρ taken as a stationary random force.

Equation (17) is now identical in form to the GLE, Eq. (4), with z and ρ replacing Z and R. The Fokker Planck equation for the action J (associated with x), Eq. (7), applies with $\mathscr{E}(J)$ now given by

$$\mathscr{E}(J) = 2\mu \sum_{n=1}^{\infty} n^2 |x_n|^2 \hat{z}_n^c \tag{27}$$

x_n is again related to the deterministic motion in $V(x)$ by Eq. (10), and

$$\hat{z}_n^c(\omega) = \int_0^\infty dt \cos(\omega t) z(t)$$

may be obtained, in terms of $Z_n(\omega)$, from Eq. (18):

$$\hat{z}_n^c(\omega) = (\mu/M_s)[n^4\omega^4\hat{Z}_n^c(\omega)] \times \{[n^2\omega^2 - (\mu/M)\omega_s^2 - n\omega(\mu/M)Z_n^s(\omega)]^2 + [n\omega(\mu/M)\hat{Z}_n^c(\omega)]^2\}^{-1} \tag{28}$$

where

$$\hat{Z}_n^c(\omega) = \int_0^\infty dt \cos(n\omega t)Z(t)$$

$$\hat{Z}_n^s(\omega) = \int_0^\infty dt \sin(n\omega t)Z(t)$$

are the real and the negative imaginary parts of

$$\hat{Z}(\omega) = \int_0^\infty dt \exp(-in\omega t)Z(t).$$

Equations (7), (27) and (28) enable us to calculate the rate of escape out of the potential well for any model defined by $V(x)$ and $Z(t)$. Consider, for example, the model characterized by a Morse function for $V(x)$:

$$V(x) = E_D[\exp(-2x/a) - 2\exp(-x/a)] \tag{29}$$

and by a choice of $Z(t)$ that yields a Debye spectrum for the motion of the surface atom in the absence of the adatom. The latter is determined by

$$\ddot{Y} = -\omega_s^2 Y - \int_0^t d\tau Z(t-\tau)\dot{Y} + (1/M_s)R(t) \tag{30}$$

which leads to (using $\langle \dot{Y}^2\rangle = kT/M_s$)

$$\hat{C}(\omega) \equiv \int_0^t dt \cos(\omega t)\langle \dot{Y}(0)\dot{Y}(t)\rangle = \frac{\omega^2\hat{Z}_1^c(\omega)(kT/M_s)}{[\omega^2 - \omega_s^2 - \omega\hat{Z}_1^s(\omega)]^2 + \omega^2(\hat{Z}_1^c(\omega))^2} \tag{31}$$

$\hat{C}(\omega)$ is related to the weighted density $g(\omega)$ of phonon modes contributing to the unperturbed motion of the surface atom by

$$g(\omega) = \frac{2M_s}{\pi kT}\hat{C}(\omega). \tag{32}$$

Thus

$$g(\omega) = \frac{2}{\pi}\frac{\omega^2\hat{Z}_1^c(\omega)}{\pi[\omega^2 - \omega_s^2 - \omega Z_1^s(\omega)]^2 + \omega^2(Z_1^c(\omega))^2}. \tag{33}$$

The function $\hat{Z}_1(\omega) = \hat{Z}_1^c(\omega) - i\hat{Z}_1^s(\omega)$ may now be determined so that $g(\omega)$ is a Debye function with a particular Debye frequency ω_D. In practice, $\hat{Z}_1(\omega)$ is chosen as an explicit function of ω with several parameters (including ω_s), and the parameters are determined to yield the best approximation to the desired Debye (or any other) form of $g(\omega)$. Finally, the functions $\hat{Z}_n(\omega) = \hat{Z}_n^c(\omega) - i\hat{Z}_n^s(\omega)$ needed in (28) are obtained using $\hat{Z}_n(\omega) = \hat{Z}_1(n\omega)$.

In this way, the functions $\hat{z}_n^c(\omega(J))$ needed in Eq. (27) and defined by Eq. (28) are obtained. The other necessary input, the functions $x_n(J)$, may be calculated explicitly for the Morse oscillator:

$$|x_n(J)|^2 = \frac{a^2}{n^2}\frac{\omega_0 J}{4E_D - \omega_0 J} \tag{34}$$

where ω_0 is the frequency at the bottom of the well. The sum in Eq. (27) may now be calculated by truncating the infinite series and summing numerically the resulting finite series. We note that the series in (27) converges everywhere for $J < J_D = 2E_D/\omega_0$.

The mean first passage time for the system to reach the threshold action J_D starting from any particular J is given by

$$\tau_{MFP}(J, J_D) = (kT)^{-1}\int_J^{J_D} dJ'[\mathscr{E}(J')]^{-1}\exp[E(J')/kT] \times \int_0^{J'} dJ'' \exp(-E(J'')/kT) \tag{35}$$

where $E(J) = \int_{J_D}^{J} dJ\omega(J)$. At steady state this has to be averaged over the steady state solution $P_{ss}(J)$ of (7), and the result constitutes the inverse escape rate calculated under the assumption that once the particle reaches the energy 0, corresponding to $J = J_D$, it escapes.

As noted elsewhere, the function $\hat{z}_n^c(\omega) = \hat{z}_1^c(n\omega)$ constitutes the classical analog to the quantum mechanical transition rate between two levels separated by the energy $n\hbar\omega$. This immediately leads to a result that suggests that the model employed here may be too limited. Since Eqs. (28) and (33) imply that $z_n^c(\omega)$ van-

ishes when $g(n\omega)$ vanishes it follows that multiphonon transitions do not contribute to the rate in this model. This result could in fact be inferred already from the structure of Eqs. (14)–(15), which show that even though the relative adatom–surface motion is nonlinear, the coupling of this motion to the rest of the lattice is linear. This stands in sharp contrast to results of other work[6] which attempt to solve Eqs. (11)–(12) without employing the transformation (13).

III. NUMERICAL RESULTS AND DISCUSSION

In order to approximately fit the properties of the noise $R(t)$ and the kernel $Z(t)$ (Eqs. (12), (30)) to a Debye model with a given Debye frequency we have used the following form for Z:

$$Z(t) = \gamma \frac{\Gamma^2 + \Omega^2}{2\Gamma}\left[\cos(\Omega t) + \frac{\Gamma}{\Omega}\sin(\Omega t)\right] e^{-\Gamma t} \quad (36a)$$

$$Z_L(\omega) = \gamma \frac{(\Gamma^2 + \Omega^2)(2\Gamma + i\omega)}{2\Gamma(\Gamma^2 + \Omega^2 - \omega^2 + 2i\Gamma\omega)} \quad (36b)$$

and determined the parameters Γ, Ω, γ and ω_s so that $g(\omega)$ (Eq. (33)) will be as close as possible to the required Debye spectrum. Such a procedure has been used before by Shugard Tully and Nitzan.[11] The resulting $g(\omega)$ is shown in the insert to Fig. 2. It is a poor approximation to the actual Debye spectrum near and beyond ω_D, but practically overlaps it at the relevant frequencies ($\omega \leqq \omega_0$, ω_0 being the frequency at the bottom of the potential $V(x)$).

In Fig. 2 we plot ln (rate) as a function of inverse temperature[12] for a model corresponding to the desorption of argon from tungsten ($M = 39.95$ au, $M_s = 183.85$ au, $E_D = 1.9$ kcal/mol, $a = 1.44$ Å^{-1}; E_D and a correspond to the Morse function (29)). The spacing between the two lowest bound levels of this system is 51 cm^{-1} compared with a surface Debye frequency of ~ 125 cm^{-1}, so that one-phonon contributions to the rate are expected to be dominant. If we analyze the straight portions of the resulting lines according to the Arrhenius form

$$k_E = \nu \exp(-E_a/kT)$$

we obtain the results summarized by Table 1. The results are given for different Debye frequencies in order to elucidate the dependence of E_a and ν on this parameter which determines the timescale for the response of the substrate. We note that if the substrate was modeled as a Markoffian thermal bath with a white phonon spectrum, Kramers' theory predicts $E_a = E_D = 1.9$ kcal/mol. The deviation of E_a from E_D is similar to that discussed by Freed, Metiu and coworkers.[6]

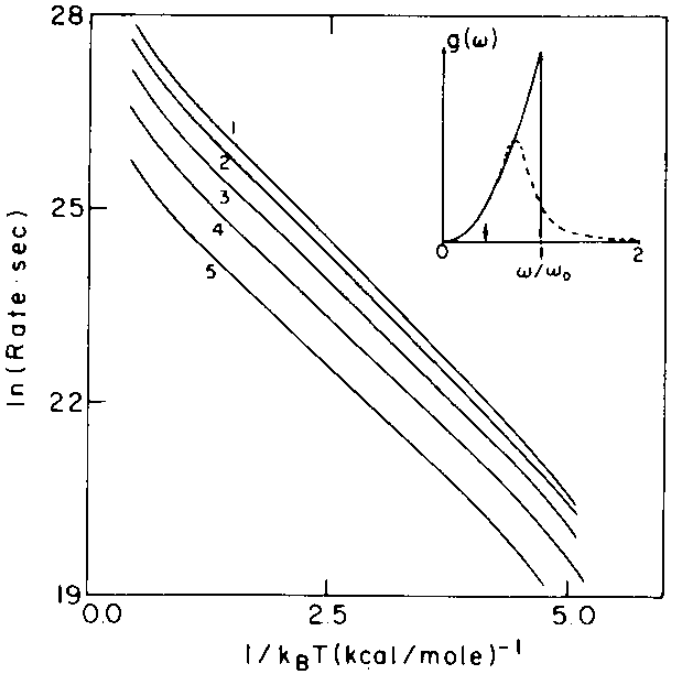

Fig. 2. An Arrhenius plot of the desorption rate for the Ar–W system with different Debye frequencies; $\omega_D \sim 125$ cm^{-1} is the surface Debye frequency of W. The insert shows the actual phonon density of states employed in the calculation, as a fit to the Debye spectrum, which is also shown. The arrow points to ω_0, the frequency at the bottom of the potential V. The five curves correspond to the different surface Debye frequencies used in Table 1 ((1) corresponds to the lowest, (5) to the highest value of ω_D).

Our results for $\omega_D = 125$ cm^{-1} should be compared to those obtained by Freed, Metiu and coworkers[6] on the same model system. Compared to their values for $\nu \sim 1.13 \times 10^{12}$ s^{-1} and $E_a \sim 1.56$ kcal/mol we get $\nu \sim 1.45 \times 10^{12}$ s^{-1} and $E_a \sim 1.70$ kcal/mol. It should be noted that the calculation in Ref. 6, in addition to the difference discussed above after Eq. (15), uses an unknown parameter, the phonon width Δ (taken tentatively to be 100 cm^{-1}), which does not appear in our calculation. The dependence of the results on this parameter makes it possible to get a better agreement between the two calculations by a somewhat different choice of Δ. The two calculations, one based on a quantum and the other on a classical picture, may thus be considered to be in good agreement. This is not too surprising: there are 25 bound levels in the potential well of this model, and a classical description should indeed work.

The situation is different for cases where multiphonon contributions are expected to be dominant, e.g., when some spacings between bound levels in the potential well are large relative to the surface Debye frequency. Here, the calculation of Ref. 6 predicts a finite rate while our calculation pedicts zero rate or a much smaller one (a non-zero contribution arises from the population in higher well levels whose spacing is small relative to the surface Debye frequency).

This drastic difference between the two calculations based on the same model is quite surprising. When a weak coupling theory is used, the definition of the coupling (that is, the way of dividing the system's Hamiltonian into $H_0 + V$ with V being the perturbation) should be expected to make a difference to the calculated transition rate unless an infinite order calculation is employed. However, both procedures used in the present work and in Ref. 6 look reasonable at first glance.

A further analysis suggests to us that our approach is generally valid, while that of Ref. 6 is valid only within the limits in which the two theories agree, that is, when

Table 1. Apparent Activation Energy E_a and Pre-exponential Coefficient ν for Argon Desorption from Tungsten (the Debye frequency associated with the substrate is varied to explore its effect on the resulting E_a and ν; the actual surface Debye temperature of tungsten is ~ 125 cm^{-1})

ω_D (cm^{-1})	E_a (kcal/mol)	ν (s^{-1})
62.5	1.75	2.05×10^{12}
125.0	1.70	1.45×10^{12}
169.0	1.67	9.22×10^{11}
214.0	1.63	4.81×10^{11}
263.0	1.40	2.27×10^{11}

multiphonon contributions may be disregarded. Consider again the procedure in Ref. 6, where the adatom–surface interaction is written as

$$V(X-Y)=\langle V(X-Y)\rangle_Y+[V(X-Y)-\langle V(X-Y)\rangle_Y]$$

$\langle V(X-Y)\rangle_Y$, an average over a thermal distribution of the surface atom coordinate Y, is taken as the zero-order Hamiltonian. In such a procedure one usually assumes that the motion associated with Y is much faster than that of X (see, e.g., the Born–Oppenheimer approximation where the fast electronic motion yields an average potential for the nuclei). This corresponds to a case where the surface Debye frequency is much larger than the frequencies associated with the potential, i.e., to a situation where single phonon effects are dominant. This suggests that for cases where multiphonon contributions are important a zero-order picture which uses the thermally averaged potential may not be justified. Another argument which points to a similar conclusion is related to the amplitudes of the thermal fluctuations: when the surface frequencies are small relative to the frequency ω_0 corresponding to the bottom of the potential $V(x)$, the amplitude for the surface motion is of the same order of magnitude as that of the adsorbed atom, and therefore treatment of the surface motion as a perturbation may not be justified.

The result obtained here should not, of course, be taken to imply that multiphonon transitions play no role in surface desorption. It does mean, however, that to calculate their effect correctly a better model should be used. Such a model should include the interaction of the adatom with more than just one surface atom, the three-dimensional nature of the motion of the adatom and, most importantly, the unharmonic nature of the lattice.

For cases where one-phonon contributions are dominant, the model used in this paper appears to be sufficient. However, care must be taken in using the low friction limit and the energy threshold criterion for desorption. If the energy criterion rate is denoted by k_E $(=[\int_0^{J_0} P_{ss}(J)\tau_{MFP}(J,J_D)dJ]^{-1})$ the actual desorption rate is

$$k_D = fk_E$$

where f is the exit probability, namely, the probability that a particle that achieved the threshold energy actually passes through x_D (see Fig. 1) without falling back to $E<0$. The validity of the energy escape criterion is thus determined by the deviation of f from unity. The quantity f itself may be determined by an independent calculation of k_D, e.g., by stochastic classical trajectories.[7] Such a test, aimed at clarifying the range of validity of the energy escape criterion, will be carried out elsewhere.

Acknowledgement. This research has been sponsored by the Commission for Basic Research of the Israel Academy of Science and by the US–Israel Binational Science Foundation. We thank U. Landman and M. Ratner for helpful discussions.

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