Quantum-mechanical rates for gas–surface processes

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Abstract

We determine exact quantum-mechanical rates for reactive scattering of hydrogen and its isotopes at and from metal surfaces. To this end, we compute cumulative reaction probabilities according to Miller, Schwartz and Tromp [J. Chem. Phys. 79 (1983) 4889], in the discrete variable representation with absorbing boundary conditions formulation of Seideman and Miller [J. Chem. Phys. 96 (1992) 4412]. In particular, canonical rates for dissociative adsorption and associative desorption of H₂ and isotopomers, as well as rates and diffusion coefficients for the diffusive motion of single hydrogen atoms on transition-metal surfaces are considered. For the adsorption/desorption processes we use various two- and three-dimensional model potential energy surfaces, which are thought to be typical for the interaction of H₂ with first-row transition metals. First for uncorrugated and rigid surfaces, the dependence of the rates on temperature(s) and potential parameters are studied. Second, we allow for non-rigidity of the substrate using the so-called surface-mass and surface-oscillator models of Luntz and Harris [Surf. Sci. 258 (1991) 397]. Further, we find that the inclusion of surface corrugation increases desorption rates, characterized by larger Arrhenius-preexponential frequencies. In our study of rates and diffusion coefficients for the hopping motion of atoms on metal substrates we focus on hydrogen on Ni(100). One- and two-dimensional realistic potential energy surfaces are used to elucidate the role of quantum effects, isotope effects, and dimensionality. We compare our results to simple quasi-classical and classical forms of transition-state theory and to experiment.

1. Introduction

The interaction of hydrogen molecules and atoms with transition-metal surfaces is of vital interest from both a technological and a fundamental point of view [1]. The former is motivated by the desire to understand the basic energetic and dynamic features, which underly many heterogeneous catalytic reactions involving hydrogen. Representative examples are the ammonia synthesis via Haber–Bosch, the synthesis of alcohols and hydrocarbons by means of the Fischer–Tropsch technique, and the steam reforming of natural gas to form so-called syngas (a mixture of H₂ and CO). The fundamental interest comes from the fact that H is the simplest chemically reacting adsorbate [2], making it a first-class candidate for the study of gas–surface scattering events.

Due to their complexity, heterogeneously catalyzed reactions are traditionally idealized as a
sequence of more or less uncorrelated elementary steps: (1) diffusion of reactants to the surface, (2) adsorption of reactants on the surface, (4) reaction, (5) diffusion of products on the surface, (6) desorption of products, and (7) diffusion of products from the surface. One typically treats these elementary reactions independently and assigns individual rate constants to each of them. Steps (2), (3) (and (5)), and (6) are peculiar to gas–surface scattering, and they are the elementary reactions which will be considered in this contribution. In fact, for certain metal-catalyzed exchange reactions, such as $\text{H}_2 + \text{D}_2 \rightarrow 2 \text{HD}$, they are the only ones.

The most complete, i.e., state-to-state description of an elementary gas–surface collision process is provided by the scattering or $S$ matrix, whose elements $\{S_{n_p,n_r}(E)\}$ are the probability amplitudes for transitions between specific quantum states $|n_r\rangle$ of reactants to specific states $|n_p\rangle$ of products at total energy $E$. In many applications, though, a less detailed knowledge of a reaction than the complete state-to-state description is sufficient. In heterogeneous catalysis, for example, the thermal rate constant,

$$k(T) = \left[\frac{2\pi\hbar}{Q_r(T)}\right]^1 \times \int_{-\infty}^{+\infty} dE \ e^{-\beta E} N(E),$$

is of great interest. Here we express this quantity in terms of the cumulative reaction probability (CRP), $N(E)$, and the reactant partition function, $Q_r(T)$. Also, $\beta = 1/k_BT$, with $k_B$ being Boltzmann’s constant and $T$ being the absolute temperature. Since the CRP is the same for a reaction and its inverse, Eq. (1.1) embodies the microscopic reversibility (or detailed balance) relation $k_{a\rightarrow b}Q_a = k_{b\rightarrow a}Q_b$. In this paper this symmetry property will be utilized for the reactions dissociative adsorption and its inverse, associative desorption. The CRP will be collectively referred to as the (dissociative) sticking probability. Further, under isothermal conditions, which are typical for technological processes, $k_{\text{ads}}(T)$ and $k_{\text{des}}(T)$ depend on only one temperature, $T$. Under laboratory conditions, however, a non-isothermal environment (with a gas temperature $T_g$ different from a surface temperature $T_s$) may be established [3,4]. In this case we expect the canonical adsorption rate, $k_{\text{ads}}$, to depend on both $T_g$ and $T_s$ (since $T_g$ governs the velocity distribution of the gas molecules and $T_s$ should have an influence on the sticking probability). In contrast the (Langmuir–Hinshelwood) desorption rate, $k_{\text{des}}$, should be a function of $T_s$ only (if thermal equilibrium between substrate and adsorbed species can be assumed). Under experimental conditions it is also possible to measure less averaged quantities than rates, for instance surface temperature and gas-energy-dependent sticking probabilities, $N(E_g, T_s)$ ($E_g$ is the normal component of the translational gas energy) [3,4]. With the help of nozzle-beam experiments it is also possible to measure half-state-selected reaction probabilities $N_{n_p}(E_g, T_s)$, by independently varying the translational beam energy and the internal reactant quantum state $|n_r\rangle$ [3,5]. Here, we will neither consider state-resolved, nor angular-resolved observables. Rather, we will restrict ourselves to cumulative reaction probabilities and quantities derived thereof.

Eq. (1.1) may also be used to characterize the kinetics of the other gas–surface process of interest in this paper, surface diffusion. Namely, the hopping of a single adsorbed molecule or atom from one stable adsorption site to another can be regarded as an isomerization reaction, characterized by a thermal rate constant, $k_{\text{diff}}$. Closely related to this quantity is a diffusion coefficient, $D$, which will, via $k_{\text{diff}}$, depend on the surface temperature $T_s$. In the case diffusion, the cumulative reaction probability thus has the interpretation of a hopping probability.

The question arises how in general the CRPs $N(E)$ are computed. $N(E)$ is defined in terms of a double sum over the square moduli of $S$-matrix elements, $N(E) = \sum_{n_p} \sum_{n_r} |S_{n_r,n_p}(E)|^2$. However, if one is interested only in the CRP and the thermal rate constant, then it is inefficient to have to compute all the state-to-state information (i.e., the $S$ matrix) first and then sum to obtain the CRP. Miller et al. [6], using flux correlation analysis, were able to derive an exact and rigorous expression for $N(E)$ which does not require the knowledge of individual $S$-matrix elements.
Instead, \( N(E) \) is expressed in terms of flux and microcanonical density operators. More recently, Seideman and Miller [7] introduced an effective implementation using a discrete variable representation (DVR [8]) for both the Hamiltonian and the flux operator, and by applying absorbing boundary conditions (ABC) [9] to enforce the outgoing wave boundary conditions. This technique has been tested for atom-exchange reactions in the gas phase [7] and applied also to a gas–surface scattering [10]. Several methodological improvements have been made, such as the implementation of an iterative method based on a Fourier transform of Newton polynomials [11] to obtain the Green’s operator (see Section 2), or the evaluation of CRPs as a sum of eigenreaction probabilities of a certain Hermitian operator [12] with the help of Lanczos-based techniques. All these techniques and their applications have shown that an efficient tool seems at hand which should make the evaluation of CRPs and quantum-mechanical rates for reactions of chemical relevance possible. Our emphasis in this paper will not be on the methodological aspects, however. Rather, we will apply the method to compute CRPs for the gas–surface processes mentioned earlier, to compute the corresponding rates and study in some detail the underlying physics.

The DVR-ABC method is not the only approach to gas–surface scattering. The computation of dissociative sticking probabilities of \( \text{H}_2 \) (which requires six degrees of freedom in the rigid surface approximation), for example has been accomplished with classical trajectory calculations [13–15] for the rigid surface case and also for moveable ones [16]. For fully quantum-mechanical investigations of the process, mostly time-dependent wave-packet propagation schemes have been employed. We mention the investigations of Jackson et al. [14,17] (mainly on \( \text{H}_2 \) on Ni(100) and Cu(100)), who included up to three degrees of freedom quantum mechanically (namely \( r \), the H–H distance; \( Z \), the molecule–surface separation; and \( \theta \), the polar angle enclosing the surface normal and the molecular axis). In a recent mixed classical–quantum scheme the remaining three degrees of freedom were treated classically [14b]. Other examples of wave-packet dynamics for gas–surface processes have been reported by Holloway et al. [18] (two-dimensional model potentials, but also realistic systems like \( \text{H}_2/\text{Cu(100)} \)), Nielsen et al. [19] (\( \text{H}_2/\text{Cu(100)} \), up to 4D), Sheng and Zhang [20] (\( \text{H}_2 \) on Ni(100), 3D), and Hand and Harris [21], who applied their surface-oscillator model (in three dimensions) also to the dissociative sticking of hydrogen on Cu. With the exception of the last paper, surface motion has rarely been included in a fully quantum-mechanical fashion. There are a few exact time-independent investigations of reactive scattering of \( \text{H}_2 \) at solid substrates. These time-independent techniques should be favorable for “slow” processes. Sheng and Zhang applied the S-matrix Kohn variational principle method [22] to \( \text{H}_2/\text{Ni(100)} \) (3D). We used the same technique and additionally the DVR-ABC method to compute sticking probabilities [10] (\( \text{H}_2 \) on model systems and Ni(100), up to 3D).

We are not aware of any work which used exact quantum mechanics to compute rates or other Boltzmann-averaged quantities relevant for dissociative adsorption or associative desorption for \( \text{H}_2/\text{transition-metal} \) systems. Approximate schemes, however, have been used. As examples we quote the contribution of Truong et al. [23], who calculated rates for the dissociative sticking of \( \text{H}_2 \) and \( \text{D}_2 \) on different Ni surfaces by means of variational transition-state theory with semiclassical tunneling corrections. Further, we mention the work of Harris et al. [24], or Brenig and Kasai [25], on surface-temperature-dependent observables relevant for associative desorption.

The reason why predominantly Ni and Cu surfaces have been considered comes from the fact that not only reliable ab initio data are available [26,27], there is also a wealth of experimental data on these systems [28,29]. It is found that for instance Ni(100) – due to vanishing activation barriers for several reaction paths – is highly reactive with respect to the dissociation of \( \text{H}_2 \). In contrast, there is a barrier of several tenths of eV for the dissociative sticking of \( \text{H}_2 \) on Cu(100), making the system less reactive. Further, the dependence of the sticking probability of \( \text{H}_2 \) on Ni(100) is found to depend only weakly on the surface temperature \( T_s \).
A comparable amount of work has been done on diffusion of H and isotopes on transition-metal substrates. Now, if surface atom motion is neglected, a theoretical description requires only 3 degrees of freedom. On the theory side, for instance, Zhang et al. used classical flux-flux and flux-position correlation functions to compute jump rates for the hopping motion of H on Ni(100) and model surfaces [30]. Again, variational transition theory with semiclassical tunneling corrections has been applied to H and isotopes on Cu [31a] and different Ni surfaces [31b,32]. Other semiclassical approaches or approximate quantum schemes were used for similar systems by Doll et al. [33], Sun and Voth [34], and Whaley and coworkers [35]. Jaquet and Miller [36] treated the hopping diffusion of H on W(100) fully quantum mechanically with the help of a Monte Carlo path integral evaluation of flux-flux correlation functions. The most complete exact quantum-mechanical investigations on H/metal diffusion have been provided by Metiu et al. Similar to Jaquet and Miller they computed diffusion (isomerization) rates as well as diffusion coefficients as the time integrals over the Miller–Schwartz–Tromp flux–flux correlation functions. They did this for H and isotopes on Cu [37a] and Ni(100) [37b]. In many of the quoted calculations surface atom motion has been included either explicitly in the form of additional degrees of freedom, or in the context of mean-field approaches.

Experimentally, diffusion rates, for instance for H and D on Ni(100), were determined in Refs. [38] and [39] for the “high-$T_s$ regime” of $> 200$ K and, recently, for the “low-$T_s$ regime” ($< 150$ K) in Refs. [40] and [41]. One finds Arrhenius behavior for the higher $T_s$, and a significant levelling off of the diffusion coefficients below $T_s \approx 130$ K or so. This behavior has been explained with a transition from an activated hopping process to a tunneling-dominated motion of hydrogen on Ni(100) [40,41].

More complete reviews on the theoretical work on adsorption, desorption and surface diffusion can be found elsewhere [42].

The paper is organized as follows. In the next paragraph (Section 2) we will review how to obtain CRPs via the DVR-ABC method, and how to proceed further to arrive at canonical rates. Section 3 deals with adsorption and desorption processes of H$_2$ and isotopomers on and from transition-metal substrates. To cover a great variety of typical H$_2$/transition-metal interactions, model potential energy surfaces will be used for this purpose and the potential parameters varied. In three subsections we will first describe the general form of adsorption and desorption rates (“Arrhenius plots”) for uncorrugated, rigid surfaces, then allow for the thermal motion of the substrate atoms (uncorrugated, non-rigid surface model), and finally study the influence of substrate corrugation (corrugated, rigid surface model). The thermal motion of the surface atoms (Section 3.2) will be treated with the help of the surface-mass model of Harris and coworkers [4]. We will find only a minor influence on adsorption and desorption rates under isothermal conditions, but a pronounced effect on adsorption rates for non-isothermal environments. Corrugation effects will simply be included by modifying the model potential energy surfaces. We will show that strong surface corrugation leads to large desorption rates, characterized by large preexponential frequency factors in the Arrhenius form of the rates. This effect is explained in similar terms as the enhancement of reaction rates in solution due to cage effects. In Section 4 we consider the hopping motion of isolated hydrogen atoms on transition metals and the rates and diffusion coefficients associated with this process. A first subsection defines the relevant quantum-mechanical quantities and their relation to simple forms of transition-state theory, a second subsection gives results for the special case of H on Ni(100). A final Section 5 concludes our work.

2. Theory

To compute canonical rates via Eq. (1.1), we need to know the reactant partition functions, $Q_r(T)$, and the cumulative reaction probabilities, $N(E)$, over which a Boltzmann average has to be performed. Since $Q_r$ and $N(E)$ are system dependent, we will keep the discussion here quite general and define specific expressions later.
For the computation of \( N(E) \) we use the DVR-ABC formulation of Seideman and Miller \[7\] to the CRP expression of Miller et al. \[6\]. Since the method has been described on several occasions \[7,10–12\], it is sufficient to list the basic equation here. We start with a formally exact expression for \( N(E) \) \[6\],

\[
N(E) = \frac{1}{2} (2\pi \hbar)^2 \cdot \text{Tr} \left[ \hat{F} \cdot \delta(E - \hat{H}) \cdot \hat{F} \cdot \delta(E - \hat{H}) \right],
\]

which derives \( N(E) \) from \( \hat{H} \) (the Hamiltonian of the system), \( \hat{F} \) (the flux operator), and \( \delta(E - \hat{H}) \) (the microcanonical density operator). By expressing the latter in terms of an outgoing wave Green’s operator \( \hat{G}(E^+) \), and \( \hat{F} \) as a commutator between \( \hat{H} \) and a Heaviside step function \( h(f(q_1, q_2, \ldots, q_F)) \) (where \( f(q) \) defines a dividing surface in \( F \)-dimensional configuration space which separates reactants from products), it can be shown that \[7\]

\[
N(E) = 4 \text{Tr} \left[ \hat{G}(E^+) \cdot \hat{\epsilon}_r \cdot \hat{\epsilon}_p \cdot \hat{G}(E^+) \cdot \hat{\epsilon}_r \right].
\]

Here,

\[
\hat{G}(E^+) = (E + i\hat{\epsilon} - \hat{H})^{-1},
\]

and \( \hat{\epsilon}_r \) and \( \hat{\epsilon}_p \) are absorbing potentials in the reactant and product regions, respectively. \( \hat{\epsilon} = \hat{\epsilon}_r + \hat{\epsilon}_p \) is the total absorbing potential. Eq. (2.3) implies that the usual convergence parameter \( \epsilon \), associated with Green’s operators, has been reinterpreted as a positive coordinate-dependent operator \( \hat{\epsilon}(q) \). \( \hat{\epsilon}(q) \) can be chosen to absorb flux exiting from the interaction such that no unphysical reflection from the boundaries of a (necessarily) finite basis function space will occur. If one introduces a not yet specific DVR for all operators, Eq. (2.2) assumes the form \[7\]

\[
N(E) = 4 \sum_j \sum_{j'} \epsilon_r(q_j) \left| G_{jj'}(E^+) \right|^2 \epsilon_p(q_{j'}),
\]

where \( \epsilon_r(q_j) \) is the magnitude of the reactant absorbing potential at grid point \( q_j = (q_{1j}, q_{2j}, \ldots, q_{Fj}) \). (Similarly, for \( \epsilon_p(q_j) \).) Further, \( G_{jj'}(E^+) \) denotes the \((j, j')\) element of the inverse of the matrix \( [\delta_{jj'}(E + i\epsilon(q_j)) - H_{jj'}] \), with the Hamiltonian matrix elements \( H_{jj'} \) given by:

\[
H_{jj'} = \sum_\alpha \sum_{\beta \neq \alpha} T_{\alpha j}^{\alpha'} \prod_{\beta = 1,\beta \neq \alpha} \delta_{jj'^\prime} + \delta_{jj'} V(q_j). \tag{2.5}
\]

(\( \delta_{jj'} \) is used as a short-hand notation for \( \delta_{jj'^\prime} \delta_{jj'^\prime'} \cdots \delta_{jj'^\prime'} \). The \( T_{\alpha j}^{\alpha'} \) are the elements of the kinetic-energy matrix, and the \( V(q_j) \) give the diagonal elements of the potential matrix). In the present paper, we will only have deal with coordinates \( q_j \in (0, \infty) \) or \( q_j \in (\infty, \infty) \). For those we adopt the evenly spaced grids proposed by Colbert and Miller \[43\] and the corresponding sinc-function-based DVR expressions for the kinetic matrix elements, Eqs. (A8) and (A7) of Ref. \[43\].

Finally, for the absorbers \( \epsilon(q_j) \) we choose, as before \[7,10\], the Woods–Saxon form

\[
\epsilon(q_j) = \frac{2\lambda}{1 + \exp\left( g(q_j)/\eta \right)}, \tag{2.6}
\]

where \( g(q_j) \) specifies the location of the absorbing potentials in configuration space, whereas \( \lambda \) and \( \eta \) determine their shape.

Once \( N(E) \) has been specified via Eq. (2.4), the Boltzmann integral Eq. (1.1) can be done numerically. To complete the computation of \( k(T) \) via Eq. (1.1), the reactant partition functions \( Q_r(T) \) are determined according to

\[
Q_r(T) = \text{Tr}[e^{-\beta\hat{H}_0}]. \tag{2.7}
\]

Here, \( \hat{H}_0 \) is some reference Hamiltonian which again depends on the particular case under consideration.

### 3. Dissociative adsorption and associative desorption

In this section, we define and compute canonical rates for the adsorption and/or desorption of \( \text{H}_2 \) and isotopomers at surfaces for three different classes of low-dimensional model potentials. These three classes represent different models for the metal surface, namely, (1) the uncorrugated, rigid model, (2) the uncorrugated, non-rigid model, and (3) the corrugated, rigid model. The present section serves not only to describe some
general features of the canonical rates, but also to examine the sometimes neglected effects of surface corrugation and thermal surface motion on physically relevant observables.

3.1. Uncorrugated, rigid surface model

3.1.1. Potential energy surfaces

For the “flat”, rigid-surface model we use two-dimensional model potentials, as originally introduced by Halstead and Holloway in their studies of dissociative adsorption of H₂ [18e]. The two degrees of freedom considered are \( r \in (0, +\infty) \) (the vibrational coordinate) and \( Z \in (-\infty, +\infty) \) (the scattering coordinate). The molecule approaches (or leaves) the surface in parallel orientation, and the four remaining degrees of freedom \( (\phi, \theta, X, Y) \) – see Ref. [10] – are kept frozen. As can be seen from Fig. 1a, there are two asymptotic channels corresponding to (1) free H₂ plus naked surface and (2) two singly adsorbed, non-interacting but nevertheless synchronically moving hydrogen atoms. These asymptotic regions are represented by one-dimensional Morse curves, each one characterized by the three parameters \( (\gamma = 1, 2 \text{ is the channel index}), D_{0\gamma} \) (well depth), \( R_{0\gamma} \) (equilibrium distance \( = R_{01} \equiv r_0 \) and \( R_{02} \equiv Z_0 \)) and \( \alpha_\gamma \) (potential range parameter). For simplicity we choose [18e] for the dynamical relevant quantities \( D_{01} = D_{02} = 4.76 \text{ eV} \) and \( \alpha_1 = \alpha_2 = 1.028 \text{ a.u.}^{-1} \). (For \( r_0 \) and \( Z_0 \) we take 1.4 a.u., though this choice has no influence on the dynamics results.) I.e., we consider classically thermoneutral reactions and use the same shape for both asymptotic potentials with parameters characteristic for free H₂. In Section 3.3 we will slightly relax this somewhat unrealistic restriction. The two asymptotes are then smoothly connected in the quarter-circular interaction region 3 via a Morse curve with the same parameters. Finally, the template is superimposed with a Gaussian form in the interaction region to establish a barrier towards dissociation of H₂ and recombination of two singly chemisorbed H atoms, respectively. The Gaussian barrier also depends on three parameters, namely \( \phi_0 \), giving its location space, \( V_0 \), determining the height, and \( \beta \), a barrier-thickness parameter (see caption to Fig. 1). By varying these parameters, one may cover a wide range of possible H₂/transition-metal interactions.

3.1.2. Hamiltonians and rates

To compute rates via Eq. (1.1) in the 2D flat, rigid surface model we have to define the Hamiltonians \( \hat{H} \) (to compute the cumulative reaction probabilities via Eqs. (2.2) and (2.3)) and \( \hat{H}_0 \) (to compute the reactant partition functions \( Q_{\text{ads}} \) and \( Q_{\text{des}} \), respectively).
Clearly,
\[ \hat{H} = -\frac{\hbar^2}{2\mu_g} \frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2M_g} \frac{\partial^2}{\partial Z^2} + V(r, Z), \quad (3.1) \]

and
\[ \hat{H}_0^{\text{ads}} = -\frac{\hbar^2}{2\mu_g} \frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2M_g} \frac{\partial^2}{\partial Z^2} + \lim_{Z \to \infty} V(r, Z), \quad (3.2a) \]
\[ \hat{H}_0^{\text{des}} = -\frac{\hbar^2}{2\mu_g} \frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2M_g} \frac{\partial^2}{\partial Z^2} + \lim_{r \to \infty} V(r, Z). \quad (3.2b) \]

Here, \( \mu_g = \frac{1}{2} m_H \) and \( M_g = 2m_H \) are the vibrational and translational gas masses for \( H_2 \) adsorption (desorption) (\( m_H \) is the hydrogen mass).

With the help of Eqs. (1.1) and (2.7) we thus obtain for the rates:

\[ k_{\text{ads}}(T_g) = \left[ 2\pi \hbar Q_{\text{ads}}(T_g) \right]^{-1} \times \int_{-\infty}^{+\infty} dE_v^{\text{tot}} e^{-\beta_g E_v^{\text{tot}}} N(E_v^{\text{tot}}), \quad (3.3a) \]
\[ k_{\text{des}}(T_s) = \left[ 2\pi \hbar Q_{\text{des}}(T_s) \right]^{-1} \times \int_{-\infty}^{+\infty} dE_v^{\text{tot}} e^{-\beta_s E_v^{\text{tot}}} N(E_v^{\text{tot}}), \quad (3.3b) \]

where

\[ Q_{\text{ads}}(T_g) = Q_{\text{ads}}^{\text{tr}}(T_g) Q_{\text{ads}}^{\text{vib}}(T_g), \quad (3.4a) \]
\[ Q_{\text{des}}(T_s) = Q_{\text{des}}^{\text{tr}}(T_s) Q_{\text{des}}^{\text{vib}}(T_s), \quad (3.4b) \]

with the translational (per unit length) and vibrational partition functions \( Q^{\text{tr}} \) and \( Q^{\text{vib}} \) given by:

\[ Q_{\text{ads}}^{\text{tr}}(T_g) = \frac{1}{2\pi \hbar} \left( 2\pi M_g/\beta_g \right)^{1/2}, \quad (3.4c) \]
\[ Q_{\text{des}}^{\text{tr}}(T_s) = \frac{1}{2\pi \hbar} \left( 2\pi \mu_g/\beta_s \right)^{1/2}, \quad (3.4d) \]
\[ Q_{\text{ads}}^{\text{vib}}(T_g) = \sum_v e^{-\beta_g \varepsilon_v^{\text{ads}}}, \quad (3.4e) \]
\[ Q_{\text{des}}^{\text{vib}}(T_s) = \sum_v e^{-\beta_s \varepsilon_v^{\text{des}}}. \quad (3.4f) \]

(With \( \varepsilon_v^{\text{ads}} = \varepsilon_v^{\text{ads}}(\mu_g) \); \( \varepsilon_v^{\text{des}} = \varepsilon_v^{\text{des}}(M_g) \); \( \beta_v \equiv 1/\hbar k_B T_v \) (\( v = g, s \)).)

Note that in our 2D model both rates are given in units of length per time, i.e. they are a measure for the change of molecules (atoms) per time, if all concentrations (of gas molecules, adsorbed atoms, and free lattice sites) are given in units of length. Further, in this model \( k_{\text{ads}} \) depends only on the gas temperature \( T_g \), whereas \( k_{\text{des}} \) is a function of surface temperature \( T_s \) only, i.e., we assume that the free gas molecules are in thermal equilibrium with a bath held at \( T_g \), whereas the adsorbed gas atoms are thermalized with the surface.

### 3.1.3. Results

Before we present some results based on the rate expressions Eqs. (3.3), a few words about numerical details and the accuracy of our calculations are in order. For the 1D bound-state calculations necessary to evaluate the vibrational contributions to the partition functions, we used the sinc-function-based DVR of the Hamiltonian as proposed in Ref. [43] with very small grid spacings and considered eigenvalues up to \( E = 3.33 \) eV. For the 2D scattering calculations to obtain \( N(E_v^{\text{tot}}) \) we used an energy-dependent grid spacing for gas energies \( E_v^{\text{tot}} \geq 0.3 \) eV, \( \Delta_e = 2\pi \hbar/[n_B(2m_H E_v^{\text{tot}})^{1/2}] \), \( \Delta_z = \Delta_e/2; \) \( n_B \), the number of grid points per deBroglie wavelength, was chosen to be 4.0 [43]. For lower gas energies, we did not further decrease the grid spacing to avoid unphysical oscillations in the low-energy tails of \( N(E_v^{\text{tot}}) \). Points with potential energies \( V > 1.7 \) eV were discarded. \( N(E_v^{\text{tot}}) \) was calculated at approximately 100 energy points in the energy range from \( \varepsilon_0^{\text{ads}} \) (i.e., the lowest vibrational eigenvalue of the free molecules) to about 1.3 eV. Further, the absorbing potentials Eq. (2.6), required in Eqs. (2.3) and (2.4), were chosen as before [10], i.e., we used 1D absorbers in the reactant and product regions. (\( g(r, Z) = Z_{\text{max}} - Z \) if \( Z > r \), and \( g(r, Z) = r_{\text{max}} - r \) if \( r < Z \); \( r_{\text{max}} = Z_{\text{max}} = 7.5 \) a.u.) The Woods–Saxon parameter \( \eta \) (Eq. (2.6)) was taken as \( \eta = 0.35 \) a.u. The second ABC parameter, \( \lambda \), turned out to have a strong influence on the (very small – in the order of \( 10^{-10} \)) cumulative reaction probabilities at the
lowest translational energies. In obtaining low-temperature rates these low-energy CRPs are multiplied with large Boltzmann factors, making the rates sensitively dependent on the ABC parameters in the low-T region. We experimented with fixed and energy-dependent $\lambda$ values, and obtained more stable results with the latter. Above $T \approx 120$ K, however, we found that the rates became insensitive to details of the absorbing boundary conditions. Below, only results in this “safe” $T$ range will be reported. All parameters were well converged and computed quantities should be as accurate as a few percent.

To establish a feeling for the relation between adsorption and desorption rates in the flat, rigid surface model, in Fig. 2 we give the ratio of these quantities, $k_{\text{des}}(T)/k_{\text{ads}}(T)$, as a function of the gas temperature $T_g$ for $T_s = 700$ K. Three different barrier parameter sets are used (see text).

![Fig. 2. Ratio of adsorption and desorption rates in the flat, rigid surface model (Eqs. (3.3)) as a function of gas temperature $T_g$ (K) for $T_s = 700$ K. Three different barrier parameter sets are used (see text).](image)

As a first feature we note that for most gas temperatures $k_{\text{des}} < k_{\text{ads}}$, in particular, at the isothermal point ($T_s = T_g = 700$ K), $k_{\text{des}} \approx 0.2 k_{\text{ads}}$. Therefore, desorption should be typically much slower than adsorption under isothermal conditions. In fact, for the 2D model potential used here, after approximating the Morse potentials in the adsorption and desorption channels by harmonic oscillators with fundamental frequencies $\omega_{\text{ads}}$ and $\omega_{\text{des}}$, an analytic expression for the ratio $k_{\text{des}}(T)/k_{\text{ads}}(T)$ (which depends only on the partition functions) can be given:

$$\frac{k_{\text{des}}(T)}{k_{\text{ads}}(T)} = \sqrt{\frac{M_g}{\mu_g}} \sinh\left(\frac{\beta h \omega_{\text{des}}}{2}\right) \sinh\left(\frac{\beta h \omega_{\text{ads}}}{2}\right).$$

Since for our model potential $M_g = 4\mu_g$ and $\omega_{\text{des}} = \omega_{\text{ads}}/2$, it is easy to show that in the limit $\beta \to 0$ (i.e., $T \to \infty$) one gets $\lim_{\beta \to 0} [k_{\text{des}}(T)/k_{\text{ads}}(T)] = 1$ and, similarly, $\lim_{\beta \to \infty} [k_{\text{des}}(T)/k_{\text{ads}}(T)] = 0$ in the low-T limit. We have seen this behavior also numerically. For more realistic systems, for which typically $\omega_{\text{des}}(T) < \omega_{\text{ads}}(T)$, the ratio in the high-T limit will typically be even $< 1$, whereas the low-T limit is unaltered. Therefore, one must, in order to clean the surface from adsorbates, establish that $T_s > T_g$. This effect, thermal desorption, is as a second feature also demonstrated in Fig. 2: only for $T_s \ll T_g$ becomes the rate of desorption larger than the rate for adsorption. The third observation to make is that at the isothermal point at $T = 700$ K all three model potentials give the same ratio $k_{\text{des}}/k_{\text{ads}}$. This is because at $T_s = T_g$ the ratio becomes independent of details of the interaction region, since owing to the principle of detailed balance the Boltzmann integrals over the CRPs are exactly the same for the forward and the backward reactions.

Next, we examine the general form of the rate expressions and their dependence on potential energy parameters. We do this via Arrhenius plots, i.e., $\ln k(T)$ versus $1/T$. Fig. 3a gives the corresponding functions for adsorption and desorption for a representative set of barrier parameters ($\phi_0 = \pi/4$, $\beta = 1.0$, and $V_0$ took values of 0.15, 0.30, and 0.50 eV.)

As a first feature we note that for most gas temperatures $k_{\text{des}} < k_{\text{ads}}$; in particular, at the isothermal point ($T_s = T_g = 700$ K), $k_{\text{des}} \approx 0.2 k_{\text{ads}}$. Therefore, desorption should be typically much slower than adsorption under isothermal conditions. In fact, for the 2D model potential used here, after approximating the Morse potentials in...
that at high $T$, as expected, the reactions follow approximately an exponential Arrhenius rate law. The third observation clearly demonstrates the importance of quantum effects for $\text{H}_2$ surface scattering. The effect of tunneling is more important for adsorption than for desorption, because the zero-point energy for desorbing reactants is in this model only half the value for the adsorbing reactants. Therefore, the recombining adsorbed atoms “see” a broader and higher barrier than the adsorbing $\text{H}_2$ molecules do, and tunneling becomes less pronounced.

Quantum effects play also a less dominant role if the gas molecules are heavier. Fig. 3b compares Arrhenius plots for the adsorption of $\text{H}_2$, $\text{D}_2$, and $\text{T}_2$, and the same model potential as before. If one determines Arrhenius activation energies $E_a$ from the slopes of the $\ln k$ curves in the high-$T$ regions, one obtains $E_a(\text{H}_2) = 310.5 \text{ meV}$, $E_a(\text{D}_2) = 322.7 \text{ meV}$, and $E_a(\text{T}_2) = 325.7 \text{ meV}$. This trend mainly reflects differences in the zero-point energies for the adsorbing free molecules, which decrease with increasing mass.

Finally, we studied the effects of variations in the potential barrier parameters $\phi_0$, $V_0$, and $\beta$. In Fig. 3c, for example, adsorption rates for $\text{H}_2$ and early ($\phi_0 = 0$), central ($\phi_0 = \pi/4$), and late ($\phi_0 = \pi/2$) barriers [18e] are compared ($\beta = 1.0$ and $V_0 = 0.30 \text{ eV}$ in all cases). Due to the release of zero-point energy along the paths from reactants to products, the effective barriers become smaller the later the barrier is located, despite the fact that the $V_0$ values are the same. Consequently, $k_{\text{ads}}(\phi_0 = 0) < k_{\text{ads}}(\phi_0 = \pi/4) < k_{\text{ads}}(\phi_0 = \pi/2)$ at most temperatures. We also observe a strong dependence of the amount of tunneling on $\phi_0$, characterized for instance by the crossing of the “central” and “early” rate curves in the tunneling region.

Besides varying the barrier location $\phi_0$ at constant $V_0$ and $\beta$, we also varied the barrier height $V_0$ ($V_0 = 0.15, 0.30, \text{ and } 0.50 \text{ eV at constant } \phi_0 = \pi/4, \beta = 1.0$) as well as the barrier-thickness parameter $\beta$ ($\beta = 0.5, 1.0, 1.5$ at constant $V_0 = 0.30 \text{ eV and } \phi_0 = \pi/4$). We find that already a moderate increase in $V_0$ leads to a distinct decrease of the rates over the full $T_g$ range. This is demonstrated in the left half of Table 1, which gives adsorption rates for different $T_g$ and $V_0$. Also a smaller $T_g$ range in which tunneling seems significant is observed. Further, the dependence of adsorption rates on $\beta$ is small, except at the lowest temperatures, where a significant increase of the (tunneling) rate with decreasing barrier thickness becomes apparent. This is demonstrated in the right half of Table 1. Results for desorption are not given here – they reflect basically the same trends.

The relevance of the last paragraph lies in the fact that for real transition metals indeed a wide range of interaction parameters is realized. As an example we mentioned in Section 1 the barrier height $V_0$ and its dependence on the particular transition metal. Further, “early” barriers (from the point of view of dissociative adsorption) for example are expected if the adsorption is very exothermic, because then the transition state should be reactant-like. Therefore, if simple arguments give already an idea how the barrier region looks like, our analysis may be used to estimate the (kinetic) reactivity of certain transition-metal surfaces.

<table>
<thead>
<tr>
<th>$T_g$ (K)</th>
<th>$V_0 = 0.15 \text{ eV}$</th>
<th>$V_0 = 0.30 \text{ eV}$</th>
<th>$V_0 = 0.50 \text{ eV}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta = 1.0$</td>
<td>$\beta = 0.5$</td>
<td>$\beta = 1.0$</td>
<td>$\beta = 1.5$</td>
</tr>
<tr>
<td>165</td>
<td>2.27 (-1)</td>
<td>4.25 (-5)</td>
<td>4.60 (-9)</td>
</tr>
<tr>
<td>625</td>
<td>7.56 (+1)</td>
<td>6.05 (0)</td>
<td>1.77 (-1)</td>
</tr>
<tr>
<td>1125</td>
<td>2.61 (+2)</td>
<td>6.27 (+1)</td>
<td>8.60 (0)</td>
</tr>
</tbody>
</table>

Table 1
Dependence of adsorption rates (in m/s – powers of ten are given in brackets) at three different gas temperatures on the barrier parameters $V_0$ and $\beta$ for the central barrier case; in the left half of the table, $V_0$ is varied at fixed $\beta = 1.0$, whereas in the right half $\beta$ is varied at fixed $V_0 = 0.30 \text{ eV}$.
3.2. Uncorrugated, non-rigid surface model

So far the surface temperature entered our analysis only in a very ad hoc fashion in the form of Eq. (3.3b). We now go beyond this somewhat phenomenological approach and introduce a microscopic model, in which surface-temperature dependence is a consequence not only of the dependence of the partition functions and Boltzmann factors on $T_s$, but rather makes the sticking probability a function of $T_s$. The so-called surface-mass model was introduced by Luntz and Harris [4c] as a simplified version of the higher-dimensional surface-oscillator model [4]. Both approaches were used to resolve some contradictory opinions on the role of tunneling played by alkanes during their dissociative adsorption on transition metals. They were also applied to other systems [4a].

### 3.2.1. Hamiltonians, $T_s$-dependent sticking probabilities, and rates

In the surface-oscillator model, the $Z$ component of the molecule’s center-of-mass motion is considered to be coupled to the acoustic motion (perpendicular to the surface) of the closest surface atom with mass $M_s$. The latter is described by a single, 1D Einstein (i.e. harmonic and monochromatic) oscillator, such that the Hamiltonian for a diatom approaching a surface in parallel orientation becomes [4]:

$$
\hat{H} = \frac{\hbar^2}{2 \mu_g} \frac{\partial^2}{\partial r^2} + \frac{\hbar^2}{2 M_s} \frac{\partial^2}{\partial Z^2} - \frac{\hbar^2}{2 M_s} \frac{\partial^2}{\partial S^2} + V(r, Z - S) + \frac{1}{2} M_s \omega_z^2 S^2.
$$

(3.6)

Here, $\omega_z$ is the harmonic frequency for the vibration of $M_s$ relative to the fixed surface, $Z$ is the distance between molecule and the fixed surface, and $S$ denotes the distance between $M_s$ and the fixed surface. Consequently, $Z - S$ is the distance between the moving surface atom and the molecule. Note that in Eq. (3.6) the additional approximation has been made, that the interaction potential $V$ depends only on $Z - S$ (and $r$), i.e., there is no distortion of the interaction potential due to surface atom motion. With the help of Eq. (3.6) one can now compute half-state-selected sticking probabilities $N_s(E^{\nu*})$, labelled by a particular surface-oscillator quantum number $\nu$. These may then be used to form an ensemble average over the oscillator states to give $N(E,$
$T_s$) - an important quantity, as mentioned earlier.

Since in this work we do not compute state-resolved information, we used Eq. (3.6) only to compare to some results obtained with the surface-mass model. In the surface-mass model, which has its roots in classical approaches to atom–surface scattering [44], the Hamiltonian takes the form [4c]:

$$\hat{H} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2\mu_{sg}} \frac{\partial^2}{\partial (Z-S)^2} + V(r, Z-S), \quad (3.7a)$$

where $1/\mu_{sg} = 1/M_g + 1/M_s$. One may think of Eq. (3.7a) as being the limit of Eq. (3.6) as $\omega_s \to 0$. The physical assumptions underlying Eq. (3.7a) are that (1) the surface atom motion is of large amplitude and "soft", and that (2) details of the surface–surface interactions do not really matter. In other words, the surface atom $M_s$ is considered as a particle which moves freely with velocity $v_s$. Sticking probabilities computed from Eq. (3.7a) are given as a function of the relative translational energy

$$E_{rel} = \frac{1}{2}\mu_{sg} v_s^2 = \frac{1}{2}\mu_{sg} (v_s - v_g)^2$$

$$= \frac{1}{M_g + M_s} \left[ M_s E_g + M_g E_s - 2(E_g + E_s) \right]^{1/2}, \quad (3.7b)$$

rather than the total energy $E$. Here $E_g = \frac{1}{2}M_g v_g^2$ is the (normal component of the) translational energy of the gas molecules with mass $M_g$ (similarly for $E_s$) and $v_{rel}$ is the velocity of gas molecules relative to the surface mass. For the surface masses, we assume a 1D Boltzmann distribution $f(v_s)$ for free particles,

$$f(v_s; T_s, M_s) = \sqrt{\frac{M_s \beta_s}{2\pi}} e^{-\beta_s M_s v_s^2/2}. \quad (3.7c)$$

One may now average over all $v_s$ to define a surface temperature and translational gas-energy-dependent sticking probability $N(E_g, T_s)$.

$$N(E_g, T_s) = \int_{-\infty}^{+\infty} dv_s f(v_s) N(E_{rel})$$

$$= \sqrt{\frac{\beta_s}{4\pi}} \int_0^\infty dE_s e^{-\beta_s E_s} N(E_{rel}). \quad (3.8)$$

In practice, $N(E_g, T_s)$ is evaluated by first specifying $E_g$ and $T_s$, then scanning over $v_s$ to determine different $E_{rel}(v_s, E_g)$, and then using a third-order spline interpolant to determine $N(E_{rel})$ at the corresponding $E_{rel}$. (The CRPs computed earlier are usually given at different $E_{rel}$ than the ones required in Eq. (3.8).) Finally, the integration is done numerically. Luntz and Harris, in their original treatment [4c], used an asymmetry factor for Eq. (3.8) to account for differences in the sticking probability due to the "upward" or "downward" motion of the surface mass $M_s$. We do not do so because this asymmetry must be already contained in $N(E_{rel})$. In numerical simulations it also turned out that for all cases studied, the influence of such an asymmetry factor was negligible.

Before we study some properties of $N(E_g, T_s)$, let us derive expressions for rates within the surface-mass model. The kinetic equations characterizing the adsorption process of a diatomic $A_2$, for example, are in the isothermal case ($T_s = T_g = T$):

$$\frac{d[A-S-A]}{dt} = k_{ads}[A_2][S]$$

$$- \sum_f \sum_{i} k_{fi,ads}[A_2][S]$$

$$= \sum_f \sum_{i} k_{fi,ads} e^{-\mu_{p,b}} [A_2][S], \quad (3.9a)$$

where $[A_2]$, $[S]$, and $[A-S-A]$ are the concentrations of free molecule, empty adsorption sites, and dissociatively adsorbed molecules, respectively. As usual, one introduces state-to-state rate
constants \(k_{fi}\), sums over all initial and final quantum states \(i\) and \(f\), and populates the initial (in this case only vibrational) states \(i\) of \(A_2\) molecules, according to a Boltzmann law. The \(k_{fi,ads}\) are given as an ensemble average

\[
k_{fi,ads} = \langle v_{rel} P_{fi} \rangle = \langle v_{rel} | S_{fi} |^2 \rangle \quad (3.9b)
\]

over relative velocities times state-to-state transition probabilities \(P_{fi}\) (which can in turn be expressed in terms of \(S\)-matrix elements). If we take the ensemble to be the canonical one, we get

\[
k_{fi,ads} = \frac{1}{2\pi h Q_{tg}^tr} \sum_f \sum_i \int_{-\infty}^{+\infty} dE_{rel} e^{-\beta E_{rel} P_{fi}}, \quad (3.9c)
\]

with

\[
Q_{tg}^tr = \frac{1}{2\pi h} (2\pi \mu_{tg}/\beta)^{1/2}. \quad (3.9d)
\]

Finally, plugging Eq. (3.9c) into Eq. (3.9a) gives

\[
k_{ads}(T) = \frac{1}{2\pi h Q_{tg}^tr Q_{tg}^{vib}} \int_{-\infty}^{+\infty} dE \ e^{-\beta E} N(E). \quad (3.10)
\]

(With \(E \equiv E_{rel} + \epsilon_{ads}\), \(N(E) \equiv \sum_f \sum_i P_{fi}(E)\), and \(Q_{tg}^{vib}\) given by Eq. (3.4e).)

The derivation of rate expressions for non-isothermal environments is less straightforward because (1) it is unclear what the ensemble average Eq. (3.9b) should be and (2) the occurrence of two different temperatures prohibits steps analogous to those leading from Eqs. (3.9a) and (3.9c) to Eq. (3.10). (The latter containing only CRP, and no state-resolved information.) However, if we take \(\langle v_{rel} P_{fi} \rangle\) to be

\[
\langle v_{rel} P_{fi} \rangle \equiv \left\langle v_g \left[ \int_{-\infty}^{+\infty} dv_{f} f(v_f) P_{fi} \right] \right\rangle \quad (3.11)
\]

(i.e., we first canonically average over \(v_g\) and then over \(v_f\)) and restrict ourselves to temperatures, where only one open channel is significant (i.e., only one initial state summand), then we obtain

\[
k_{ads}(T_s, T_g) = \frac{1}{(2\pi h)^2 Q_{tg}^tr Q_{tg}^{vib}(T_s) Q_{tg}^{vib}(T_g)} \times \frac{1}{\sqrt{\frac{M_s}{2}}} \int_{0}^{\infty} dE_{g} \ e^{-\beta E_{g}^tot} \times \int_{0}^{\infty} dE_{s} \ e^{-\beta E_{s}} \ N(E_{rel}). \quad (3.12)
\]

(The molecular vibrational and translational partition functions are given by Eqs. (3.4e) and (3.4e); \(Q_{tg}^tr = (1/2\pi h)(2\pi M_s/\beta)^{1/2}; \quad E_{g}^tot = E_{g} + \epsilon_{ads}\).) Similar expressions, both for the isothermal as well as non-isothermal cases, may be derived for the desorption processes.

3.2.2. Results

Before we compute canonical rates via Eq. (3.10), let us consider the surface-temperature-dependent sticking probabilities, \(N(E_{rel}, T_s)\). In particular, we start with the \(M_s\) dependence of these quantities at a constant surface temperature. In Fig. 4a, we give \(T_s\)-dependent sticking probabilities as a function of the total (translational plus vibrational) energy of the gas molecules, \(H_v\), as obtained from Eq. (3.8). The different curves, which are compared to the rigid surface model, are for different surface masses \(M_s\) entering the surface-mass Hamiltonian, Eq. (3.7a). We used 2D model potentials of the type described earlier, with \(\phi_0 = \pi/4, V_0 = 0.30 \text{ eV}\), and \(\beta = 1.0\). To arrive at these curves, the integral had been evaluated at \(\sim 2000 \mu_s\) points. The non-interpolated \(N(E_{rel})\) was computed at \(\sim 150\) energies. We were choosing a surface temperature low enough to ensure that the observed effects are really due to mass differences, but at the same time high enough to avoid numerical problems associated with the integral (3.8) at low \(T_s\).

We see from Fig. 4a that the cumulative reaction probability curve of the rigid surface model (Eq. (3.11)) is (1) shifted to higher energies and (2) appears to be somewhat flattened, if finite surface masses are used. The effects are the larger,
Fig. 4. Cumulative, surface-temperature-dependent sticking probabilities in the surface-mass model (Eq. (3.8)). (a) Dependence of \( N(E_g, T_s) \) for \( \text{H}_2 \) on the surface mass \( M_s \) at \( T_s = 20 \) K. (b) Dependence of \( N(E_g, T_s) \) for \( \text{H}_2 \) on the surface temperature \( T_s \) at \( M_s = 10m_{\text{H}} \). \( E_p \) denotes the isoprobabilistic point.

Fig. 4b shows \( \text{H}_2 \) \( N(E_g, T_s) \) curves, again as a function of total gas energy, for different surface temperatures \( T_s \) (\( T_s = 100, 600, \) and 1100 K) and the same potential parameters. We choose \( M_s = 10 \) hydrogen masses, since for masses characteristic for transition metals (45–65\( m_{\text{H}} \)) the results are qualitatively the same, but less pronounced. Compared to the rigid surface case, which is also given in Fig. 4b, the following four features associated with the surface-mass model can be realized. (1) There is a shift of the curves relative to the rigid surface case to higher energies. The shifted curves are centered approximately around an energy \( E_p \). (2) For \( E < E_p \), the sticking probabilities are increased relative to the (shifted) rigid curve and decreased for \( E > E_p \). (3) These effects are the more distinct, the higher \( T_s \). (4) \( E_p \) is an isoprobabilistic point with sticking probabilities independent of surface temperature.

The shift of all \( N(E) \) curves is easily explained with arguments similar to the ones employed in connection with the \( M_s \) dependence of \( N(E_g, T_s) \). Namely, also for \( T_s \rightarrow 0 \) the Boltzmann distribution goes over into a delta function. But now,

\[
\lim_{T_s \rightarrow 0} N(E_g, T_s) = N(\frac{1}{2} \mu_{eg} v_g^2)
\]

is not approaching the rigid surface value, \( N(E_g) \), since the reduced mass \( \mu_{eg} \) is smaller than the \( \text{H}_2 \) molecular mass (as long as not \( M_s \rightarrow \infty \)). The
hence smaller energy argument in \( N(E) \) causes a shift of \( N(E) \) to higher energies. This observation has already been made by Hand and Harris \([4a]\) and attributed by them to the recoil of a stiff and moveable barrier by an impinging molecule.

Topics (2) (for the \( E < E_p \) branch at least) and (3) were interpreted by the same authors as surface “thermally assisted tunneling” \([4]\). Though the extent of tunneling, which is significant for the dissociation of \( \text{H}_2 \) on rigid metals \( (N(E_g) \) is non-negligible even for \( E_g < V_0 \)), might in fact change due to the surface atom motion, the observed effects of non-rigidity of the substrate can also be explained on purely classical grounds. Namely, for the surface-mass model in its classical limit the sticking coefficient below the multiple open channel region is, at constant \( E_g \), a Heaviside step function in the surface atom velocities:

\[
N(E_{\text{rel}}) = h(v_s - v_s^0; E_g),
\]

and Eq. (3.8) becomes

\[
N(E_g, T_s) = \sqrt{\frac{m_s \beta_s}{2\pi}} \int_{v_s^0}^{v_s^\infty} dv_s \ e^{-\rho_s M_s v_s^2/2}. \quad (3.15b)
\]

This integral gives rise to smoothed step functions like the ones in Fig. 4b. They rise quickly from 0 to 1 if \( T_s \) is low, and more slowly for large \( T_s \). Further, if \( v_s^0 \) (the surface atom velocity, for which the \( T_s \)-independent sticking probability \( N(E_{\text{rel}}) \) jumps from 0 to 1) is 0, the integral Eq. (3.15b) is \( \frac{1}{2} \) and independent of \( T_s \). This is close to what one observes in Fig. 4b. The \( v_s = 0 \) condition allows us also to compute the isoprobabilistic energy point \( E_p \). Namely, for \( v_s = 0 \) and a classical treatment the relative energy \( E_{\text{rel}} \) must be equal to \( V_0 \), the classical barrier height. Using Eq. (3.7b) together with this condition gives:

\[
E_p = V_0 - \frac{M_g + M_s}{M_s}. \quad (3.15c)
\]

Since \( (M_g + M_s)/M_s > 1 \), \( E_p \) is typically larger than the classical barrier value. This shows again that (and by how much) the surface-mass model curves are shifted to higher energies.

The behavior indicated in Fig. 4b is not only important as a theoretical concept, but has experimental significance. For instance, Michelsen et al. \([29f]\), who used phenomenological forms for the sticking probabilities of \( \text{D}_2 \) on Cu(111) to explain certain adsorption and desorption data, were able to reproduce the angular dependence of desorbing flux only after introducing \( T_s \)-dependent \( N(E) \) curves. Form and features of these curves were quite similar to what we described in connection with Fig. 4b.

Therefore, the surface-mass model seems to have a reasonable physical basis and the question arises how it compares to its higher-dimensional (but not necessarily physically more motivated) counterpart, the surface-oscillator model. In Table 2 we compare sticking probabilities at some selected energies as obtained with the rigid surface model, the surface-mass model, and the surface-oscillator model. For the surface-mass model calculations, which give reaction probabilities as a function of \( E_g \) and \( T_s \), we took \( T_s = 20 \) K, i.e. a very low surface temperature to make the comparison meaningful. We note that the different non-rigid surface models agree well with each other, in particular at higher energies. By varying the surface-oscillator parameters in Eq. (3.6), we

### Table 2

Comparison of sticking probabilities obtained with the rigid surface model (Eq. (3.1) – first row, “rigid”), the surface-mass model (Eqs. (3.7a) and (3.8) at \( T = 20 \) K – second row, “SM”), and the surface-oscillator model (Eq. (3.6) with \( \omega_s = 30 \) meV – third row, “SO”); for the non-rigid models \( M_s = 50m_H \) was taken, the barrier parameters for the 2D model potential were \( V_0 = 0.20 \) eV, \( \beta = 1.0, \phi_0 = \pi/4 \)

<table>
<thead>
<tr>
<th>( E_g^\text{tot} ) (eV)</th>
<th>0.37</th>
<th>0.39</th>
<th>0.41</th>
<th>0.43</th>
<th>0.45</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rigid</td>
<td>0.227 (-2)</td>
<td>0.179 (-1)</td>
<td>0.128 (0)</td>
<td>0.541 (0)</td>
<td>0.863 (0)</td>
</tr>
<tr>
<td>SM</td>
<td>0.101 (-2)</td>
<td>0.563 (-2)</td>
<td>0.366 (-1)</td>
<td>0.205 (0)</td>
<td>0.580 (0)</td>
</tr>
<tr>
<td>SO</td>
<td>0.869 (-2)</td>
<td>0.225 (-1)</td>
<td>0.527 (-1)</td>
<td>0.181 (0)</td>
<td>0.604 (0)</td>
</tr>
</tbody>
</table>
- rigldllliace

--- surfacemassmodel,  
Ms=50, Ts=100K

--- surface mass mod& Ms=50, Ts=GOOK

14.0 2.0 4.0 6.0 8.0

Inverse Gas Temperature (1/Tg)/(1/1000K)

8.0

Fig. 5. Arrhenius plots for the rates of adsorption in the surface-mass model. Barrier parameters are \( \phi_0 = \pi /4 \), \( V_0 = 0.30 \text{ eV} \), \( \beta = 1.0 \). (a) \( k_{\text{ads}} (T) \) (Eq. (3.10)) under isothermal conditions \( T_s = T' = T \), for \( M_s = 10m_\text{H} \) (dotted) and \( M_s = 50m_\text{H} \) (dashed), as compared to the rigid surface rate (Eq. (3.3a)) (solid). (b) Adsorption rates for \( \text{H}_2 \) under non-isothermal conditions as a function of gas temperature \( T_g \) (Eq. (3.12)). The rigid surface result (solid line) is compared to surface-mass rates for \( T_s = 100 \text{ K} \) (dot-dashed) and \( T_s = 600 \text{ K} \) (dashed).

found for many cases only very small differences to the data shown here; in others, however, the surface-mass and surface-oscillator models were only in qualitative agreement with each other. Nevertheless, the basic trends due to surface atom motion should be accounted for by the surface-mass model.

We now come to the computation of rates in the surface-mass model. In Fig. 5a we show Arrhenius plots for the dissociative adsorption of \( \text{H}_2 \) under isothermal conditions. We took potential-energy parameters as before \( \phi_0 = \pi /4 \), \( V_0 = 0.30 \text{ eV} \), \( \beta = 1.0 \) and surface masses of \( M_s = 50m_\text{H} \) and \( M_s = 10m_\text{H} \), respectively. One immediately realizes that the inclusion of substrate motion leads to only very small changes in the rates, in particular for surface masses which are more typical for transition metals. The trend can be easily understood with reference to Fig. 4a.

From Fig. 4b, however, one expects much larger effects on the rates of adsorption under non-isothermal conditions. In fact, we find, using Eq. (3.12) (Fig. 5b) a pronounced effect for \( k_{\text{ads}} (T_g, T_s) \) if \( T_g \neq T_s \). For very low surface temperatures (e.g., \( T_s = 100 \text{ K} \)), the non-rigid model adsorption rates are smaller than the “rigid ones” over the full \( T_g \) range. For higher surface temperatures (e.g., \( T_s = 600 \text{ K} \)), the low-\( T_g \) regime is characterized by larger, and the high-\( T_g \) regime by lower rates than in the rigid case. Since Eq. (3.12) can be viewed as a Boltzmann average over \( T_g \)-dependent sticking probabilities Eq. (3.8), these results may be easily understood with reference to Fig. 4b.

By substituting \( \text{H}_2 \) with \( \text{D}_2 \), we observed that the effects on sticking probabilities and rates became somewhat more pronounced, i.e., the inclusion of substrate atom motion is more important if heavier gas isotopes are considered. In particular, the low-\( E \) sticking probability increased more for \( \text{H}_2 \) than for \( \text{D}_2 \) if surface motion was included. This effect was used by Luntz and Harris to identify a direct, tunneling-mediated dissociative adsorption mechanism for alkanes on transition metals as more important than a precursor-mediated alternative [45].

3.3. Corrugated, rigid surface model

Besides substrate atom motion, a second surface effect which is sometimes neglected is surface corrugation. Here we include corrugation effects for the desorption process only, since the barrier region and, therefore, the cumulative reaction probability should not strongly depend on surface corrugation. In fact, as long as only adsorption/desorption processes are considered and not their coupling to diffusive atom motion, this is a very reasonable approximation [10]. However, the partition functions for the desorption process do strongly depend on corrugation. Hence, for all
corrugation models employed below we will use the same sticking probabilities as for the flat surface case (with the proper barrier parameters, of course) and obtain different desorption rates only via different $Q_s(T_s)$.

3.3.1. Potential energy surfaces

To include corrugation, we still use the 2D model potential surfaces of previous sections, but allow for a periodic variation with H–H distance $r$ of the desorption channel Morse parameters $D_{02}$, $\alpha_2$, and $Z_0$ (see Section 3.1.1):

$$\tilde{D}_{02} = D_{02} - \frac{D_d}{2} \left( 1 - \cos \frac{\pi r}{a} \right),$$

$$\tilde{\alpha}_2 = \alpha_2 - \frac{\alpha_d}{2} \left( 1 - \cos \frac{\pi r}{a} \right),$$

$$\tilde{Z}_0 = Z_0 - \frac{Z_d}{2} \left( 1 - \cos \frac{\pi r}{a} \right).$$

Here, $a$ is the lattice constant, which we will also refer to as the “corrugation parameter”, since for $a \to \infty$ the flat surface model is gained back. The quantities with subscript “d” are correction terms which ensure that at $r = 2a$, $4a$, $6a$, etc. (i.e., at the chemisorption minima) for instance the Morse well depth is $\tilde{D}_{02} = D_{02}$, whereas for $r = a$, $3a$, $5a$, etc. (i.e., at the transition states for the simultaneous diffusion of two single adatoms) the corresponding quantity is $\tilde{D}_{02} = D_{02} - D_d$. For realistic H$_2$/transition-metal systems $D_d$ is in the order of 1 eV and below, $Z_d$ is in the order of $-1$ a.u. or less, and $-\alpha_d$ is in the order of a few tenth of a.u.$^{-1}$ or so. I.e., in going from one adsorption minimum to the next a barrier has to be crossed with atom–surface distances usually slightly increasing and the atom–surface vibrations becoming “harder”. In most of the following studies we choose for the diffusion parameters $D_d = 1.0$ eV, $Z_0 = 0.0$ a.u., and $\alpha_d = -0.5$ a.u.$^{-1}$. The corresponding potential energy surface is shown in Fig. 1b. We will show that varying these parameters in reasonable intervals does not change the results very much.

3.3.2. Hamiltonians and rates

As noted earlier, we use the same sticking coefficients for the flat and corrugated surface models. Hence, the Hamiltonian $\hat{H}$ is the same as in Eq. (3.1).

The reference Hamiltonian $\hat{H}_0^{\text{des}}$ for desorption, however, is not any longer given by Eq. (3.2b). Namely, if corrugation is introduced the formerly free relative translation of the two adsorbed atoms becomes a hindered one. Eventually, at low enough temperatures the adsorbed atoms will be trapped in the corrugation wells. In this case the reactant partition function $Q_r^{\text{des}}$ can be evaluated from a 2D bound state calculation with Hamiltonian

$$\hat{H}_0^{\text{des}} = -\frac{\hbar^2}{2\mu_g} \frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2M_g} \frac{\partial^2}{\partial Z^2} + V(r, Z),$$

which is the same as the one in Eq. (3.1), except that in practice we now restrict the configuration space to the region of the first well shown in Fig. 1b and place hard walls outside. I.e., $r \in (0, 2a)$ and $Z \in (-\infty, +\infty)$. We have extensively tested this approximation by extending the configuration space and varying other computational parameters and found that, up to temperatures of about 800 K, the partition function $Q_r^{\text{des}}$ changes by less than 10%. In other words, at these temperatures two singly adsorbed hydrogen atoms are in fact trapped in adjacent sites, vibrating relative to each other and – correlated – relative to the surface.

Therefore, the rate for desorption can be written as

$$\tilde{k}_\text{des}(T_s) = \left[ \beta_\nu / \left( 2\pi \mu_g \sum_{\nu=0}^{\infty} e^{-\beta \epsilon^{\text{des}}_\nu} \right) \right] \times \int_{-\infty}^{+\infty} dE_g \text{tot} \ e^{-\beta \epsilon^{\text{tot}}_g} N(E_g^{\text{tot}}),$$

where the tildes indicate that in contrast to Eq. (3.3b) the rates are now given in units of time$^{-1}$ and are derived from 2D vibrational energies $\tilde{\epsilon}^{\text{des}}_\nu$. I.e., the rates measure now the production of free molecules per time, where the concentrations of adsorbed gas particles are given in units of particles per site. To compare to the desorption rates for flat surfaces, which measured the change of molecules per length per time with
adsorbed species given per length, we define also a desorption rate \( k_{\text{des}} \) according to
\[
k_{\text{des}}(T_s) = \tilde{k}_{\text{des}}(T_s) a. \tag{3.18b}
\]

Here, the partition functions are per unit length and, therefore, rates are given in units of length per time.

### 3.3.3. Results

In Fig. 6 the Arrhenius plots for desorption rates \( k_{\text{des}}(T_s) \) (Eq. (3.18b)) in the temperature range from 125 to 725 K are shown. The different curves correspond to different corrugated surface models, characterized by different lattice spacings \( a \). (The other corrugation parameters \( D_d, \alpha_d, Z_d \) were chosen as described above and the Gaussian barrier parameters were \( \phi_0 = \pi/4, V_0 = 0.50 \text{ eV}, \beta = 1.0 \).) A lattice parameter of \( a = 3.5 \text{ a.u.} \) is typical for the well–well separations on a (111) surface of a typical transition metal with fcc structure, \( a = 5 \text{ a.u.} \) is characteristic for the (100) face, and \( a = 7.0 \text{ a.u.} \) is representative for the longer basis vector of a (110)-indexed crystal face. The larger \( a \)'s are just to demonstrate the transition from the corrugated to the flat surface case.

From Fig. 6 we note that, provided the other potential parameters are the same, the rate for desorption \( k_{\text{des}} \) increases considerably with decreasing corrugation parameter \( a \) and finally approaches the flat surface result. The latter observation is purely a consequence of the fact that the partition function for the 2D oscillator divided by the lattice constant \( a \), approaches the product of the partition functions of the 1D oscillator Eq. (3.4f), and the relative translational partition function, as given in Eq. (3.4d). Further, a tunneling region at low (surface) temperatures and an Arrhenius behavior at higher \( T_s \) is again observed.

This remains also true if \( \ln \tilde{k}_{\text{des}} \) (Eq. (3.18)) versus \( 1/T_s \) curves, which we do not show here, are considered. The Arrhenius expression for the associative desorption from a corrugated surface is
\[
\tilde{k}_{\text{des}}(T_s) = \nu_0 e^{-\beta \Delta E_a}, \tag{3.19}
\]
with \( \nu_0 \) denoting the attempt frequency for the “recombinative mode” and \( E_a \), the activation energy for this reaction. (\( E_a = V_0 \) for a classical, thermonutral process without zero-point restrictions.) Table 3 gives the Arrhenius parameters \( E_a \) and \( \nu_0 \), as extracted from the high-\( T_s \) regime of Eq. (3.18). First we note that the activation energies approach a value of \( E_a \approx 586 \text{ meV} \), which is larger than the classical barrier height, \( V_0 = 500 \text{ meV} \), and smaller than the flat surface value of \( E_a \approx 592 \text{ meV} \). This reflects mainly the differences in the zero-point energies of reactants and transition-state-like arrangements. Namely, because zero-point energies for a 2D oscillator are

---

### Table 3

<table>
<thead>
<tr>
<th>( a ) (a.u.)</th>
<th>( E_a ) (meV)</th>
<th>( \nu_0 ) (s(^{-1}))</th>
<th>( \Delta \nu ) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>533.4</td>
<td>1.86 (13)</td>
<td>3.31 (13)</td>
</tr>
<tr>
<td>5.0</td>
<td>572.1</td>
<td>1.01 (13)</td>
<td>8.46 (12)</td>
</tr>
<tr>
<td>7.0</td>
<td>580.3</td>
<td>5.90 (12)</td>
<td>5.56 (12)</td>
</tr>
<tr>
<td>10.0</td>
<td>583.7</td>
<td>3.60 (12)</td>
<td>1.26 (12)</td>
</tr>
<tr>
<td>15.0</td>
<td>585.7</td>
<td>2.19 (12)</td>
<td>6.29 (11)</td>
</tr>
</tbody>
</table>

\( ^{a} \) The \( \approx \) value is extracted from the flat surface result Eq. (3.3b).
larger than for its 1D counterpart, for the highly corrugated surfaces the reactants “start” from levels with higher vibrational energy. Second, the attempt frequencies decrease rapidly with increasing corrugation parameters. This shows that the recombinative mode becomes more and more translational. At the same time, the perpendicular mode does not change much. The attempt frequency scales roughly with the difference between the ground-state-level energies for the 2D oscillator, \( \varepsilon_{0}^{\text{des}} \), and the 1D oscillator \( \varepsilon_{0}^{\text{des}} \) which arises from \( a \to \infty \), multiplied by the appropriate factors:

\[
\Delta \nu = \frac{1}{\pi \hbar} (\varepsilon_{0}^{\text{des}} - \varepsilon_{0}^{\text{des}}).
\]  

(3.20)

\( \Delta \nu \) is given in Table 3 as a measure for the frequency of the recombinative vibration. (If the 2D oscillator were an uncoupled, harmonic one, \( \Delta \nu \) would be the fundamental frequency for the associative mode.)

In summary we note that both effects, the high zero-point energy as well as the high attempt frequency (which are interconnected quantities) contribute to large desorption rates for the highly corrugated surfaces. This is quite similar to what is known in solution dynamics under the name cage effect: if the reactants are effectively trapped in a cage formed by solvent molecules, the relative translation is hindered, the attempt frequencies are high, and the rate constants are large. In our case the corrugated surface plays the role of a solvent cage. The magnitude of this effect might be diminished if higher-dimensional models are employed, where trapping is expected to be less pronounced.

We also varied the parameters defining the well in which the hydrogen atoms are trapped and studied their effect on the desorption rates. Actually, in our 2D model potential, there are two sets of parameters responsible for the corrugation well regions, namely the “diffusion” parameters \( D_{d}, \alpha_{d}, \) and \( Z_{d} \), and the “chemisorption well” parameters \( D_{02}, \alpha_{2}, \) and \( Z_{0} \).

In varying the former parameters in large ranges around the reference values used above, we found that the effects on \( \tilde{k}_{\text{des}} \) were very small, in particular in the high-\( T_{s} \) region. At \( T_{s} = 145 \) K and \( a = 5.0 \) a.u., for example, \( \tilde{k}_{\text{des}} \) changes from \( 1.10 \times 10^{-3} \) to \( 0.94 \times 10^{-3} \) s\(^{-1} \) (if \( D_{d} \) changes from \( 1.0 \) to \( 0.5 \) eV), or to \( 1.08 \times 10^{-3} \) s\(^{-1} \) (if \( \alpha_{d} \) changes from \( -1.0 \) to \( 0.0 \) a.u.\(^{-1} \)), and finally to \( 1.12 \times 10^{-3} \) s\(^{-1} \) (if \( Z_{d} \) changes from \( 0.0 \) to \( -1.0 \) a.u.). In other words, the shape of the desorption well is not altered too much by varying the diffusion parameters, such that the 5 vibrational eigenvalues or so, which contribute significantly to \( Q_{r}^{\text{des}} \) in the considered \( T_{s} \) range, are not much affected. The largest effect is found for the \( D_{d} \) parameter, and, in fact, if this parameter became very small, the adsorbed particles were not trapped anymore and, therefore, the rates would decrease more strongly than observed here. In that sense, below a certain threshold, \( D_{d} \) can play a similar decisive role as the corrugation parameter \( a \).

One expects the vibrational eigenvalues to depend more strongly on the chemisorption parameters. We varied \( D_{02}, \alpha_{2}, \) and \( Z_{0} \) and observed (using still the same sticking probabilities as earlier – an approximation not quite as good as before) only a weak dependence of desorption rates on \( Z_{0} \), but a distinct change if \( D_{02} \) or \( \alpha_{2} \) were varied. For instance, at \( T_{s} = 295 \) K, the desorption rates drop from \( 2.72 \times 10^{3} \) to \( 0.18 \times 10^{3} \) s\(^{-1} \) (if \( \alpha_{2} \) changes from \( 1.028 \) to \( 0.514 \) a.u.\(^{-1} \)) and even to \( 0.17 \) s\(^{-1} \) (if \( D_{02} \) changes from \( 4.76 \) to \( 5.01 \) eV). These potential parameters are characteristic for a distinct exothermic adsorption process, like \( \text{H}_2 \) on \( \text{Ni}(100) \). For this system the chemisorption well is deep and broad (in the \( Z \) direction), favoring many low-lying vibrational levels contributing to \( Q_{r}^{\text{des}} \), and thus reducing \( k_{\text{des}} \). In particular the well depth parameter plays an important role, mainly because the barrier “seen” by the associating atoms changes significantly. More quantitative conclusions, however, should only be given after recalculating the cumulative reaction probabilities, because varying the chemisorption parameters usually also leads to a distortion of the barrier region.

4. Diffusion processes

The last gas–surface process for which quantum-mechanical rates and related quantities are
computed here, is the diffusion of H atoms and isotopes on a Ni(100) surface. This section is mainly to demonstrate the performance of the DVR-ARC method for diffusion events. Hence, we will restrict ourselves to low-dimensional models (1D and 2D) and not include substrate mobility or multiple jumps. For a discussion of the problems associated with the definition of diffusion constants under these idealized conditions see, for instance, Refs. [30,37].

4.1. Hamiltonians, rates, and diffusion coefficients

Let \( z \in (-\infty, +\infty) \) be the location of the adatom perpendicular to the surface, and \( x, y \in (-\infty, +\infty) \) denote in-plane degrees of freedom, then the Hamiltonian for the motion of H on this surface is

\[
\hat{H} = -\frac{\hbar^2}{2m_H} \left( \frac{\delta^2}{\delta x^2} + \frac{\delta^2}{\delta y^2} + \frac{\delta^2}{\delta z^2} \right) + V(x, y, z).
\]

(4.1a)

The form of lower-dimensional (1D and 2D) Hamiltonians is obvious. In practice we do not cover infinite space, but rather enclose a certain volume of configuration space with imaginary absorbing potentials. In the 1D case (the \( x \) coordinate, say), for example, one may place absorbers at \(-x_{\text{max}}\) and \(+x_{\text{max}}\) and then obtain hopping probabilities for one-, two-, three-, \ldots, \( N \)-fold jumps, depending on how many barriers lie in the \([-x_{\text{max}}, +x_{\text{max}}]\) interval.

This physical picture makes sense only if the reactants can be considered as localized within one adsorption well. Similar to the desorption of \( \text{H}_2 \) from a corrugated surface, this is true for low enough temperatures only. Then the reference Hamiltonian determining \( \mathcal{Q}_r^{\text{diff}}(T_s) \) can be approximated by

\[
\hat{H}_0^{\text{diff}} = \hat{H}.
\]

(4.1b)

with \( x \) and \( y \), however, being confined to the dimensions of one elementary cell. Hence, for a quadratic lattice with lattice constant \( a: z \in (-\infty, +\infty), x \in (-a/2, +a/2), \) and \( y \in (-a/2, +a/2) \).

Once CRPs via Eq. (4.1a) and partition functions via Eq. (4.1b) have been determined, canonical rates \( k_{\text{diff}}(T) \), characterizing a (single) jump process or isomerization reaction, may be computed using Eq. (1.1):

\[
k_{\text{diff}}(T_s) = \left( \frac{2\pi \hbar \mathcal{Q}_r^{\text{diff}}}{E_g^{\text{tot}}} \right)^{-1} \times \int_{-\infty}^{+\infty} dE_g^{\text{tot}} e^{-\beta E_g^{\text{tot}}} N(E_g^{\text{tot}}) \sigma. \quad (4.2)
\]

Here, \( E_g^{\text{tot}} \) is now the total energy of the adsorbed atom and \( \sigma \) is a degeneracy factor counting equivalent final sites.

Further, if the coverage of adsorbed species is low, and if the diffusion can be viewed as a series of uncorrelated hops characterized by the unimolecular rate \( k_{\text{diff}} \) within a random-walk model, then diffusion coefficients \( D \) can be defined [33]

\[
D(T_s) = \frac{b^\gamma}{2\gamma} k_{\text{diff}}(T_s), \quad (4.3)
\]

with \( \gamma = 1, 2, \) and 3 for chain, surface, and bulk diffusion, respectively. (The jump length \( b \) equals \( a \) for single jumps on quadratic lattices.)

As an alternative to the quantum-mechanical rate expressions, rates derived from transition-state theory [46] are frequently used for surface-diffusion processes [31,32]. In a simple form of transition-state theory, the rate for single jumps (in \( x \) direction, say) over a barrier of height \( V_0 \) is [47,48]

\[
k_{\text{diff},\text{TST}}(T_s) = \frac{\gamma}{2\pi \hbar \beta_s} \frac{Q_x^* Q_y^*}{Q_r^{\text{diff}}} e^{-\beta_s F_s} \mathcal{Q}_r^{\text{diff}}. \quad (4.4a)
\]

where \( Q_x^* \) and \( Q_y^* \) are the partition functions for the perpendicular modes at the transition state and \( F_s \) is an activation energy including zero-point corrections. Eq. (4.4a) becomes for a 1D model:

\[
k_{\text{diff},\text{TST}}(T_s) = \frac{1}{2\pi \hbar \beta_s} \frac{1}{Q_x^*} e^{-\beta_s E_s}, \quad (4.4b)
\]

where \( Q_x \) is the reactant partition function \( Q_r^{\text{diff}} \) for one dimension, resulting from the trapped vibration in \( x \) direction. Exactly the same expression Eq. (4.4b) results from the form Eq. (4.2) if the classical limit for the hopping probability is
taken. Namely then \( N(E_{F}^{\text{tot}}) = h(E_{F}^{\text{tot}} - E_{\text{g}}) \) and the integral Eq. (4.2) can be done analytically to give Eq. (4.4b). As a first estimate to diffusion coefficients, sometimes even the high-\( T \) or classical limit to the reactant partition functions is used, for which

\[
\lim_{T_{s} \to \infty} k_{\text{diff,TST}}(T_{s}) = (2\pi \hbar \beta, \nu_{0})^{-1}
\]

and [47,48]

\[
\lim_{T_{s} \to \infty} k_{\text{diff,TST}}(T_{s}) = \nu_{0} e^{-\beta_{s} \nu_{0}}.
\]  \hspace{1cm} (4.4c)

Eq. (4.4c) is identical to an Arrhenius expression for the hopping rate, with \( \nu_{0} \) now having the interpretation of an attempt frequency for the hopping in \( \pm x \) direction. Of course one may also give an Arrhenius expression to the diffusion coefficient itself, i.e.

\[
D(T_{s}) = D_{0} e^{-\beta_{s} \nu_{0}}.
\]  \hspace{1cm} (4.5)

The simplified expression Eq. (4.4b) (in which quantum effects enter only via the partition functions) and Eq. (4.4c) (which is a fully classical expression) will be compared to the quantum rate, Eq. (4.2) below.

4.2. Hydrogen on Ni(100)

4.2.1. Potential energy surface

For our study of hydrogen motion on Ni(100) we use a 6D London–Eyring–Polanyi–Sato (LEPS) potential energy surface in the parametrization we proposed earlier [10]. This surface was based on ab initio as well as experimental data with the aim to realistically describe the atop approach of \( \text{H}_{2} \) to Ni(100). We can use it also for diffusion processes, by “infinitely” separating the first hydrogen atom from the second one. I.e., we choose the \( r, \theta, \phi, X, Y, \) and \( Z \) degrees of freedom (see Fig. 1 of Ref. [10]) as follows: \( r \to \infty, \theta = 0, \phi \) arbitrary; \( X = x, Y = y, \) and \( Z = z + r/2 \) are then varied to give a 3D potential energy \( V(x, y, z) \) as required for Eq. (4.1a). To obtain a realistic potential not only for the atop approach of the diatom, but also for the diffusive motion of single atoms, two of the potential parameters listed in the appendix of Ref. [10], namely \( a_{02} \) (which now is \(-0.1440337\) instead of \(-0.1317716\)) and \( b_{02} \) (which now is \(0.4015248\) instead of \(0.3458333\)) had to be adjusted [49].

Below we will work only with one- and two-dimensional cuts through the surface, however. Fig. 7 shows contours of the 2D \( \text{H}-\)surface potential characteristic for the hopping of \( \text{H} \) on Ni(100) from one center (i.e., a fourfold-hollow) position to a neighbouring one via a bridge position, i.e., \( y \) was fixed at \( y = a/2 = 1.24 \, \text{Å} \). This process, which is the most important one for the diffusion of \( \text{H} \) on Ni(100), will be referred to here as the center–bridge–center or c–b–c pathway.

A one-dimensional model of the c–b–c isomerization can be generated by constructing a 1D minimum energy path from the 2D c–b–c potential. We found that this 1D potential curve, along which \( z \) changes but \( y = a/2 \), can accurately be parametrized by (apart from a constant shift):

\[
V(x) = \frac{V_{0}}{2} \cos \frac{2\pi x}{a}.
\]  \hspace{1cm} (4.6)

In the 1D c–b–c model, therefore, the reactant wells in the center sites \( x = \pm a/2, \pm 3a/2, \pm 5a/2, \cdots; a = 2.48 \, \text{Å} \) are separated by barriers of height \( V_{0} \) at the bridge positions \( x = 0, \pm a, \pm 2a, \pm 3a, \cdots \), where \( V_{0} = 0.155 \, \text{eV} \).

4.2.2. Results

As a first check of the DVR-ABC technique as applied to diffusive problems we did not start with H/Ni(100), but rather compare the method
with data of Haug et al. [37a] on H/Cu(100). As noted earlier, these authors employed quantum-mechanical flux-flux time-correlation functions. Using their one-dimensional “1Dxa model” we found reasonable agreement between this and the present treatment. For instance, at \( T_s = 300 \) K, Haug et al. give a diffusion coefficient derived from single jumps, \( D = 8.01 \times 10^{-7} \) cm\(^2\)/s, whereas we find \( D = 8.22 \times 10^{-7} \) cm\(^2\)/s.

Next, the 1D c-b-c model for H/Ni(100) was considered. As noted earlier, the proper definition of the partition functions \( Q_{\text{eff}}^{\text{diff}} \) is a serious problem, except at low enough temperatures. For a single well of the 1D c-b-c potential Eq. (4.6), there are 5 highly localized states with energies < 0.155 eV. Above this energy, the density of states becomes much larger and sensitive to computational parameters and eventually a continuum of states is formed. At temperatures below 450 K or so, however, these higher and delocalized states contribute less than 5% to \( Q_{\text{eff}}^{\text{diff}} \). (This can be easily checked by changing the value for the highest energy included in the summation of \( Q_{\text{eff}}^{\text{diff}} \).) Therefore, the particle indeed appears to be trapped. As in Section 3, there is also a lower bound to this “safe” \( T_s \) regime, due to the sensitivity of the CRPs at low \( T_s \) on details of the absorbing potentials. Again, we give only results for the unproblematic \( T_s \) range from 125–450 K. For D and T a single well supports 6 and 8 bound states, respectively, and the safe \( T_s \) range is approximately the same.

In Fig. 8a we give the natural logarithm of the 1D, single-jump diffusion coefficients \( D \) (Eq. (4.3a) with jump length \( b = a = 2.48 \) Å) for H/Ni(100), D/Ni(100), and T/Ni(100) as a function of reciprocal temperature. We note that for all temperatures \( D(H) > D(D) > D(T) \), since the

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Fig. 8. Arrhenius plots for diffusion coefficients \( D(T_s) \) for hydrogen on Ni(100). (a) Quantum-mechanical single-jump diffusion coefficients (from rate Eq. (4.2)) for H (solid), D (dashed), and T (dot-dashed) in the 1D c-b-c model. (b) Comparison between single-jump diffusion coefficients, as obtained with the quantum rates Eq. (4.2) (very thick lines), the quasi-classical TST rates Eq. (4.4b) (thick lines), and the classical TST rates Eq. (4.4c) (thin lines). The full lines are for H, the dot-dashed ones are for T. In all cases the 1D c-b-c model is employed. (c) Comparison between quantum theory and experiment for H and D. For the theory curve, 1D c-b-c and 2D c-b-c models have been used.
zero-point energies of the lighter atoms are higher and also tunneling is more favored. Tunneling effects decrease with increasing isotope mass, as can be seen from the slope of the curves. Again there is an Arrhenius region at higher surface temperatures.

Fig. 8b shows once more the quantum-mechanical diffusion coefficients $D$ for $H$ and $T$. Additionally, for each isotope two curves are given which correspond to the $D_s$ obtained from the quasi-classical and classical transition-state theory (TST) rate expressions (4.4b) and (4.4c). First we mention that the TST diffusion coefficients are lower than the quantum-mechanically derived quantities. This is due to the absence of tunneling in Eqs. (4.4). Therefore, one often corrects expressions like (4.4a) with a tunneling factor. Second, the quasi-classical and classical TST results approach each other at higher $T_s$, because the classical partition function then approaches the quantum-mechanical one. Third, at higher $T_s$ the TST coefficients become also similar to the fully quantum results, since tunneling corrections are less pronounced for higher $T_s$. Finally, the TST approximations are better for the heavier isotope then for the lighter one.

If we determine Arrhenius parameters $\nu_0$ and $E_a$ to the quantum (Eq. (4.2)) and quasi-classical (Eq. (4.4b)) rate expressions, and compare it to the fully classical treatment Eq. (4.4c), the role of tunneling versus zero-point corrections can be studied separately. (Of course this is only true in 1D – in higher dimensions recrossing effects and less predictable zero-point corrections will complicate the analysis.) For instance, for the activation energies $E_a$ we find: $E_a$ (quantum) = 141.8 meV, $E_a$ (quasi-classical) = 147.1 meV for H; $E_a$ (quantum) = 148.2 meV, $E_a$ (quasi-classical) = 150.9 meV for D; $E_a$ (quantum) = 149.3 meV, $E_a$ (quasi-classical) = 151.2 meV for T. Of course the purely classical value is $E_a = V_0 = 155.0$ meV.

Both zero-point and tunneling corrections tend to decrease this classical value. The zero-point (plus partition function) corrections are, as can be seen from the $E_a$ (quasi-classical) data, in the order of 4–8 meV, where the lower value is for T, and the larger is for H. The role of tunneling is estimated via computing $\Delta E_a = E_a$ (quasi-classical) – $E_a$ (quantum) to give $\Delta E_a = 5.3$ meV (H), $\Delta E_a = 2.7$ meV (D), and $\Delta E_a = 1.9$ meV (T). Similar observations made for $\nu_1$ lead to the conclusions that for this system and in the high-$T_s$ region (1) zero-point effects are slightly more important than tunneling corrections, and that (2) quantum effects rapidly decrease with adatom mass.

Finally, Fig. 8c compares computed quantum-mechanical diffusion coefficients for H and D on Ni(100) in the temperature range from 200–280 K with the experimental data of Refs. [38] and [39]. We observe a rough agreement. Arrhenius prefactors $D_0$ and activation energies $E_a$ (Eq. (4.5)) are for hydrogen: $D_0$ (theory, 1D) = $4.8 \times 10^{-3}$ cm$^2$/s; $E_a$ (theory, 1D) = 141.8 meV. The experimental values for $D_0$ in this high-$T_s$ region are scattered over a range of more than three orders of magnitude: $D_0$ (experiment) = $1.1 \times 10^{-4}$ cm$^2$/s [41] to $D_0$ (experiment) = $4.5 \times 10^{-3}$ cm$^2$/s [39], whereas the experimental $E_a$ values lie all between 139 140 meV [40, 41]. For deuterium in the high-$T_s$ region we get: $D_0$ (theory, 1D) = $3.9 \times 10^{-3}$ cm$^2$/s, $D_0$ (experiment) = $2 \times 10^{-5}$ [41] to $8.5 \times 10^{-3}$ cm$^2$/s [38]; $E_a$ (theory, 1D) = 148.2, $E_a$ (experiment) = 156 [41] to 217 meV [40].

The observation that in the 1D c–b–c model diffusion coefficients are too high is attributed to the fact that in reality the adatoms do not move along the minimum energy path only, but also populate less favorable reaction paths. This effects is demonstrated also in Fig. 8c which additionally gives the single-jump diffusion coefficients for the 2D c–b–c model, with the potential energy surface shown in Fig. 7. Now, however, the diffusion coefficients for the high-$T_s$ region are too low (compared to Refs. [38, 39] at least) and it is to be expected that inclusion of the third dimension will make things even worse. For the Arrhenius parameters extracted from the quantum model we now obtain: $D_0$ (theory, 2D) = $5.1 \times 10^{-3}$ cm$^2$/s, $E_a$ (theory, 2D) = 187.8 meV for H, and $D_0$ (theory, 2D) = $3.4 \times 10^{-3}$ cm$^2$/s, $E_a$ (theory, 2D) = 177.4 meV for D. The inclusion of the following effects, which have been shown to contribute to higher diffusion coefficients, are expected to bring our results in better agreement with experiment: (1) increased tunneling of ad-
sorbates due to substrate atom motion [31-37] and (2) contributions from multiple jumps [30,37].

The importance of tunneling manifests predominantly in the low-$T_s$ region. We observed the mentioned levelling off of the In $D$ curves at very low $T_s$, as reported in Refs. [40] and [41]. In H on Ni(100) in the 1D c--b--c model, for example, this behavior becomes distinctly apparent only below $T_s \approx 100$ K, i.e. outside the $1/T_s$-range shown in Fig. 8a. In the 2D c--b--c model the tunneling regime starts at $T_s \approx 125$ K. As in the experiments [40,41], the low-$T_s$ region is observed to be characterized by much smaller Arrhenius parameters $D_0$ and $E_a$. For H in the 2D c--b--c model, for example, $D_0$ in our calculations drops by ca. four orders of magnitude, and $E_a$ by a factor of almost three. (Again, due to the uncertainty of our low $T_s$ results, we do not make more quantitative statements here, and also do not reproduce our low-$T_s$ curves.) According to experiments performed in Ref. [40b], $D_0$ decreases by a factor of close to 1000 and $E_a$ by a factor of 2.9.

Therefore, in summary, our theoretical diffusion coefficients for the high-$T_s$ regions agree in absolute values better with Refs. [38,39]. However, the basic trends in going to lower $T_s$, as reported in Refs. [40,41], are also well reproduced.

5. Conclusions

The present work may be summarized as follows. The DVR-ABC method, which circumvents the need to determine state-to-state information to compute cumulative reaction probabilities, and, therefore, promises to make systems of chemical relevance quantum-mechanically tractable, has been applied to determine rates for gas–surface reactions. In particular, we studied the typical gas–surface processes (1) dissociative adsorption of diatoms, (2) recombinative desorption of diatoms, and (3) surface diffusion of single adatoms. All three steps are for the first time treated fully quantum mechanically and within the same methodological framework. For (1) and (2) three different surface models have been employed: (a) the uncorrugated, rigid surface model, (b) the uncorrugated, non-rigid surface model, and (c) the corrugated rigid surface model. We find that for H$_2$ and isotopomers interacting with model transition-metal surfaces, the inclusion of substrate motion has only a weak influence on canonical rates under isothermal conditions, but may have (for the adsorption process) a more distinct effect if surface and gas temperatures are not the same. Corrugation tends to enhance desorption rates due to the trapping of the reactants and, therefore, increasing the prefactor to the integral in Eq. (1.1). This is a similar effect as the cage effect known from dynamics in solution. Surface diffusion has been studied for the system H and isotopes on Ni(100) using low-dimensional models. Zero-point corrections as well as tunneling corrections turn out to be important for H, but less pronounced for heavier isotopes. (This is also true for the adsorption/desorption reactions.) Both quantum effects can separately be studied by comparing the quantum results to quasi-classical and classical forms of transition-state theory. The agreement between theory and experiment is fair, better agreement is expected if substrate motion is included.

Our analysis mainly suffers from the use of only low-dimensional models. However, the DVR-ABC technique should open the way to a more realistic treatment, and in fact our ongoing work is devoted to include additional degrees of freedom. Further, surface atom motion seems to be important under certain circumstances even for hydrogen interacting with transition metals. Simple models, like the surface-mass treatment of Luntz and Harris, are promising. Finally, though cumulative reaction probabilities are important quantities in particular for the field of heterogeneous catalysis, laboratory experiments more and more reveal half-state-selected information for gas–surface events. Again, one would like to avoid to have to compute the full state-to-state probabilities. Efficient time-independent methods to compute half-state-selected data directly, which use the same methodological ingredients as the ones employed here, have been proposed and applied to gas-phase dynamics [50,11]. The use of these methods for gas–surface studies is another route of our ongoing research.
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These parameters were obtained by deleting the ab initio data of Upton and Goddard [26e,f] from the averaging process to obtain well depths for the H-surface Morse potential. Their ab initio data seem to predict a too large difference in the energies of the bridge and center positions of 11 on Ni(100).