Diffusion on Metal Surfaces: Formalism and Application to CO Diffusion

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An analytical approach searching for the saddle point on a semiempirical adiabatic potential surface (SP-SE-APES) is proposed in order to study diffusion of adsorbed molecules on a metal surface. Three reaction coordinates are used to construct this potential surface: the perpendicular adsorption height, the distance between adsorption sites (top, bridge, or hollow), and coordinate describing phonon vibrations of the metal atoms. Harmonic approximation is used to describe the potential energy along the coordinate, and anharmonic Morse functions are used to describe the potential energies along and coordinates. The theory is applied to study CO diffusion on five transition metals (rhodium, ruthenium, palladium, iridium, and platinum), and the activation energies and the prefactors are calculated for various hopping mechanisms. The one-step top—bridge—top path with the bridge state as a transition state, which was generally assumed to be the dominant mechanism of CO diffusion on these metals, is shown not to be the most likely path. Results of calculation of the diffusion coefficients are compared with experimental data.

Introduction

The diffusion of adsorbed particles on metal surfaces has been a subject of great fundamental and technological interest for some time by now due to the crucial role that mobility plays in many processes. Most kinetic models assume that surface diffusion is much faster than the various kinetic steps and that the surface is “well mixed”, so that its steady state can be described by algebraic equations. This may not be justified in many cases. The problem may be resolved by theoretical and experimental investigation of the hopping frequency of adatoms between equilibrium positions on a surface. Theoretical approaches of various levels of sophistication (see ref 2 and references therein) were developed for describing the diffusion coefficient and its temperature dependence, which is conveniently expressed by the Arrhenius-type equation (eq 1)

\[ D = D_0 \exp\left(-\frac{E_{\text{a}}^{\text{diff}}}{k_B T}\right) \] (1)

In the framework of the theory of rate processes the prefactor \( D_0 \) has the following form,

\[ D_0 = \lambda^2 \frac{k_B T \bar{Z}}{h \bar{Z}_i} \] (2)

where \( \lambda \) is the distance between two neighboring equilibrium positions (adsorption sites), and \( \bar{Z} \) and \( \bar{Z}_i \) are the partition functions for the transition and for the initial states, respectively. When the degree of freedom corresponding to diffusion in a solid is assumed to be a vibrational one having a classical frequency, then the number of vibrational degrees of freedom in the initial state will be more than that in the transitional state by one. In this assumption the ratio \( \bar{Z}/\bar{Z}_i \) is reduced to \( h\nu/k_BT \) and eq 2 has the following form (eq 3).

\[ D_0 = \lambda^2 \nu \] (3)

For diffusion on a surface, the \( D_0 \) should be multiplied by 1/4 according to refs 2 and 4. At the next levels of sophistication, the rate of diffusion of adsorbed particles was calculated (at the zero coverage limits) as its rate of escape from a one-dimensional (1D) well using Kramers theory and then extended to two-dimensional (2D) and to three-dimensional (3D) wells, ignoring the return of adatom into the original well. Detailed consideration of the prefactors calculated in these works is beyond the scope our work and may be found in the referred papers.

A simple unit bond index-quadratic exponential potential (UBI-QEP) approach based on semiempirical calculation of the interaction between atom or certain molecular radical with several strongly localized electrons, which resemble atomic adsorbates (such as CH or CH2), and a metal surface was applied using density functional theory (DFT) methods. The energy was shown to be proportional to the corresponding adsorption energy \( (-E_{\text{a}}) \). Particularly, for face-centered cubic (fcc) surfaces it was found that

\[ E_{\text{a}}^{\text{diff}} = 0.1(-E_{\text{a}}) \] (4)

for hopping between hollow sites. This derivation assumes that the minimum energy path for diffusion proceeds via the one-step hollow—bridge—hollow mechanism and that the bridge state is a transition state. It was shown that predictions given by eq 4 for O, S, C, and N atoms adsorbed on some fcc(111) surfaces are in good agreement with those calculated using density functional theory (DFT) methods.

The assumption that the bridge state is the transition state was also used in refs 12–14 for the calculation of diffusion barriers of molecules with closed-shell molecules, such as CO. However, it seems to be not always justified, particularly for

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CO diffusion on some transition metals. It was experimentally shown\(^{15}\) that the on-top site is the most favorable one for CO adsorption on a (111) Pt surface, and the energy of bridge and hollow adsorbed CO molecules is only slightly higher than that of on-top adsorbed molecules. Meanwhile, the activation energy for CO diffusion over this surface is much higher than that of on-top adsorbed molecules. Meanwhile, the activation energy for CO diffusion over this surface is much higher than that of on-top adsorbed molecules.

In the present work we suggest an analytical approach (at the limit of zero coverage) to study surface diffusion, in which the activation energy for a hopping is found by calculation of the saddle point (SP) coordinates on the semiempirical adiabatic potential energy surface (SE-APES), and the corresponding prefactor is determined in the framework of the theory of rate process. We do not assume a preferred diffusion path but consider a hopping between the two neighboring adsorption surface states with the highest adsorption energy. This path is a sequential two-step transition via a mediated stationary state, and we calculate the partial transition probabilities for both steps. This calculation takes into account a possible back transition and the transitions into other neighboring sites. The activation energy and the prefactor of the effective diffusion coefficient are numerically calculated from the temperature dependence of the effective transition probability.

The formalism of the proposed approach is similar to that previously developed for describing chemical reactions on metal surfaces.\(^{19}\) The main advantages of our approach are as follows: (i) It does not require the laborious and computer-time-consuming numerical calculations of the total PES; only quantum chemical or experimental information about the initial and the final stationary adsorption states, given by the corresponding theory parameters, is required for calculation of the saddle point, that is, for calculation of the diffusion coefficient. Therefore, the main factors that determine the diffusion coefficient and its variation within a group of metals can be discussed by performing inexpensive calculations. (ii) The formalism accounts for a local reorganization of the metal atoms near the adsorption sites. (iii) The method provides a simple way for calculation of the transition state frequencies. The main drawback of the approach is in its approximate form of the APES.

### 1. Formalism Used for Description of the Two-step Diffusion Processes

There are four types of adsorption sites on a metal (111) surface (Figure 1): an on-top (t) site with one adatom-metal bond, a bridge site (b), with two bonds between the adatom and the metal, and hollow hcp and fcc sites (h) with three such bonds, and diffusion involves hopping between them. The preferred site depends on the nature of the metal and of the adsorbate and may change with coverage. We study the hopping between h→t, h→b, t→b, or b→b sites. For simplicity we neglect the small energetic difference between fcc and hcp adsorption sites.

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**TABLE 1: Results of Calculations of CO Diffusion over Transition Metal Surfaces**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Ru</th>
<th>Rh</th>
<th>Pd</th>
<th>Ir</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_{ads}), top</td>
<td>-31.4</td>
<td>-37.8</td>
<td>-30.7</td>
<td>-34.5</td>
<td>-30</td>
</tr>
<tr>
<td>(E_{ads}), bridge</td>
<td>-28</td>
<td>-34</td>
<td>-37.5</td>
<td>-30</td>
<td>-28.5</td>
</tr>
<tr>
<td>(E_{ads}), hollow</td>
<td>-29</td>
<td>-31.4</td>
<td>-38.5</td>
<td>-24.5</td>
<td>-28.5</td>
</tr>
<tr>
<td>(z), top</td>
<td>1.892</td>
<td>1.838</td>
<td>1.822</td>
<td>1.890</td>
<td>1.838</td>
</tr>
<tr>
<td>(z), bridge</td>
<td>1.6</td>
<td>1.550</td>
<td>1.497</td>
<td>1.580</td>
<td>1.518</td>
</tr>
<tr>
<td>(z), hollow</td>
<td>1.56</td>
<td>1.510</td>
<td>1.247</td>
<td>1.602</td>
<td>1.388</td>
</tr>
<tr>
<td>(\omega), top</td>
<td>440</td>
<td>466</td>
<td>500</td>
<td>467</td>
<td>490</td>
</tr>
<tr>
<td>(\omega), bridge</td>
<td>340</td>
<td>350</td>
<td>380</td>
<td>320</td>
<td>380</td>
</tr>
<tr>
<td>(\omega), hollow</td>
<td>330</td>
<td>340</td>
<td>370</td>
<td>311</td>
<td>370</td>
</tr>
<tr>
<td>(a)(metal–metal)</td>
<td>2.58</td>
<td>2.62</td>
<td>2.73</td>
<td>2.63</td>
<td>2.71</td>
</tr>
</tbody>
</table>

**Calculated Diffusion Characteristics**

| \(D_{diff}\), \(E_{diff}\) | 6.8 × 10^{-7} | 5.0 × 10^{-7} | 7.1 × 10^{-5} | 1.3 × 10^{-7} | 2.4 × 10^{-7} |
| \(D_{diff}\), \(E_{diff}^{k}\) | 6.0 [3.4] | 6.3 [3.8] | 2.2 [1.0] | 6.9 [4.5] | 6.4 [1.5] |
| \(E_{diff}^{k}\)/\(E_{ads}\) | 1.2 × 10^{-2} | 2.0 × 10^{-2} | 3.1 × 10^{-3} | 1.4 × 10^{-2} | 1.0 × 10^{-2} |
| \(E_{diff}^{k}/E_{ads}\) | 0.19 | 0.17 | 0.06 | 0.18 | 0.21 |

**Experimental Values**

| \(E_{diff}\) | 6.2–11\(^{c}\) | 7.1\(^{d}\) | 12.4–12.7\(^{c}\) |
| \(D_{diff}\) | 6 × 10^{-2} to 0.4\(^{c}\) | 10^{-2} to 10^{-3}\(^{d}\) | 0.6 to 1.2\(^{c}\) |

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\(^{a}\) Energies in kcal/mol, adsorption heights \(z\) and distances \(\omega\) in Ångströms, frequencies \(\omega\) in cm\(^{-1}\); \(D_{diff} = D_{diff}^{k} \times \exp\left[-\frac{E_{diff}^{k}}{kT}\right]\); \(D_{diff}\) and \(D_{diff}^{k}\) in cm\(^2\)/s; the values in square brackets were calculated under the assumption that the bridge adsorption state is the transition state for \(t \rightarrow t\) and \(h \rightarrow h\) diffusion.\(^{b}\) \(T = 300\) K; the ratio \(E_{diff}^{k}/E_{ads}\) was calculated for the most adsorption energy.\(^{c}\) Reference 17.\(^{d}\) Reference 18.\(^{e}\) Reference 13; DFT; PW91 and RPBE functionals; hcp-bridge-fcc diffusion.\(^{f}\) Reference 14; DFT; PW91/RPBE functional; top-bridge-top diffusion.\(^{g}\) Reference 12; DFT; PW91/RPBE functional.\(^{h}\) Reference 46.

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**Figure 1.** Types of adsorption sites on a (111) metal surface: t, on-top; b, bridge; f, fcc hollow; h, hcp hollow.
1.1. h-Hopping. If the energy of h-adsorbed species is lower than that of t- and b-adsorbed species, then diffusion takes place by hopping between adjacent h-sites. Such hopping may occur only via b- or t-adsorbed states, (see Figure 2). Calculating the probability of the sequential h0 → b01 → h1 transition, while accounting for the h0 → h1 distance \( \lambda = a/\sqrt{3} \) (where \( a \) is the metal–metal bond length), we find the following expression for the diffusion coefficient through the \( h \rightarrow b \rightarrow h \) mechanism (for algebraic details see Appendix A)

\[
D_{hhb} = \frac{a^2/2}{W(h0, b01)W(b01, h1) + 3W(b01, h1)} \tag{5}
\]

where \( W(j, k) \) is the hopping frequency between an \( j \) and \( k \) adsorption sites. Similarly, one may easily obtain equation for the diffusion coefficient for the \( h \rightarrow t \rightarrow h \) transition (see Appendix A)

\[
D_{htb} = a^2 \frac{W(h0, t0)W(t0, h1)}{2W(h0, t0) + W(t0, h1)} \tag{6}
\]

The diffusion coefficient involving both transition mechanisms is equal to the sum of the partial coefficients given by eqs 5 and 6.

\[
D_h = D_{htb} + D_{hhb} = a^2 W_{eff} = a^2 \times \frac{1}{2W(h0, b01)W(b01, h1)} + \frac{3W(h0, t0)W(t0, h1)}{2W(h0, t0) + W(t0, h1)} \tag{7}
\]

1.2. t-Hopping. This type of diffusion assumes that the adsorption state of an ad-species on a t-site is more stable than that on other sites of a surface. There are two possible mechanisms for adsorbed species to diffuse between the adjacent t-sites: \( t \rightarrow b \rightarrow t \) and \( t \rightarrow h \rightarrow t \) (Figure 2). Calculation of the probabilities of both two-step transitions, accounting for that the distance \( \lambda \) between neighboring t-sites is equal to \( a \), leads to eq 8

\[
D_t = a^2 \left[ 3 \frac{W(t0, b01)W(b01, t1)}{2W(b01, t0) + 3W(b01, t1)} + \frac{2W(t0, h0)W(h0, t1)}{W(t0, h0) + 2W(h0, t1)} \right] \tag{8}
\]

1.3. b-Hopping. When the b-adsorbed state is the most stable one (see Figure 2), we should consider three possible transitions \( b \rightarrow b \rightarrow t \rightarrow b \) and \( b \rightarrow t \rightarrow b \). It can be shown that the diffusivity that accounts for all three mechanisms has the following form (eq 9).

\[
D_b = a^2 \left[ W(b01, b06) + \frac{3}{4} W(b01, t0)W(t0, b06) + \frac{1}{2} W(b01, h0)W(h0, b02) \right] \tag{9}
\]

Thus, the calculation of these diffusion coefficients is reduced to the calculation of the probabilities per second (frequencies) \( W(j, k); j = h, t, b, k = b, t \). These transition frequencies are computed here using a model adiabatic potential energy surface (APES), along which an ad-particle A moves from one (initial) site to other (final) as it is shown in next section. The APES is constructed from two diabatic PESs describing the potential energies of adparticle A adsorbed at the initial and final sites of a metal.

2. Potential Surfaces and Transition Probability

The diabatic PESs are assumed to depend on the following coordinates, the equilibrium values of which vary significantly from one site to another: (1) The coordinate \( x \) describing the position of an adsorbed particle on a line connecting the neighboring adsorption sites involved in the transition; its equilibrium values are \( x_0b \) and \( x_0a \). (2) The vertical coordinate \( z \) connecting A and the metal surface; its equilibrium values are \( z_0b \) and \( z_0a \) for the initial and final states, respectively. (3) A set of coordinates \( \{r_k\} \) describing small vibrations of \( k \)-atoms of a metal near the adsorption center; the corresponding equilibrium values change from \( r_{0a} \) to \( r_{0b} \) as a result of the particle hop. The simplest form of the diabatic PESs in the two-state model corresponds to the assumption that the interaction between vibration modes along the reaction coordinates is absent\(^{19,20} \) (such interaction can, in principle, be accounted for in the formalsism\(^{21} \)).

Thus, we write the diabatic PESs of the initial and final states in the following forms,

\[
U_i = u_i(x) + v_i(z) + w_i(\{r_k\}) \tag{10}
\]

\[
U_f = u_f(x) + v_f(z) + w_f(\{r_k\}) + \Delta E \tag{11}
\]

where \( \Delta E \) is the difference of the minimum values of the \( U_i \) and \( U_f \); the minimum energy at the initial state is set to be zero. \( \Delta E \) may be interpreted as the difference of the adsorption energies of diffusing species at the initial and final adcenters. \( u_i(x) \) and \( u_f(x) \) are the potential energies of the particle adsorbed at the initial and final sites in the direction parallel to the metal surface, \( v_i(z) \) and \( v_f(z) \) are the potential energies of this particle in the perpendicular direction, and \( w_i(\{r_k\}) \) and \( w_f(\{r_k\}) \) are the potential energies for vibrations of metal atoms of the crystal lattice.

Harmonic approximation is used to analytically express the potential energies \( w_i(\{r_k\}) \) and \( w_f(\{r_k\}) \) describing small vibrations of metal atoms. In this approximation one may introduce only one effective coordinate (\( \theta \)) instead of the set \( \{r_k\}\).\(^{19,20,22} \)

Geometrically, \( \theta \) may be interpreted\(^{19} \) as a symmetry characteristic of the potential energy surface that is expressed via the slopes of the diabatic PESs \( U_i \) and \( U_f \) at the point of their intersection, and it describes the symmetry of the transition configuration of the corresponding nonadiabatic reaction. In terms of \( \theta \), the components of the PESs, \( w_i \) and \( w_f \), can be rewritten in the following simple form,
where \( E_r \) is the so-called reorganization energy,\(^{19,20,23} \) which characterizes the metal atoms displacements, as a result of the diffusion step, of the equilibrium values of coordinates of metal atoms near the adsorption center. An approximate estimation of this quantity in terms of cluster models may be obtained by the equation \((1/2)\mathcal{E} M_0 \delta (r_{at} - r_0)^2\), where \( r_{at} \) and \( r_0 \) are the metal–metal bond lengths of a metal cluster with an adsorbed atom or molecule and of a bare metal cluster and which we assign as the initial and final adsorbed states for a partial transition; \( M \) is the reduced mass of the M–M oscillator with the frequency \( \omega \). Thus, in the present model the diabatic surfaces \( U_i(x, y, \theta) \) and \( U_j(x, y, \theta) \) are in fact 3D. The specific forms of the potentials \( u_i(x), v_i(z) \) and \( u_j(x), v_j(z) \) are not of fundamental importance at a given point and will be discussed later.

Then, following a commonly used procedure,\(^22 \) we construct the adiabatic PES using the diabatic energy surfaces given by eqs 10 and 11 as follows,

\[
U = (1/2)[U_i + U_j -((U_i - U_j)^2 + 4V^2)^{1/2}] \quad (14)
\]

where \( V \equiv V(x) \) is the half-splitting of the diabatic PESs. The exact form of \( V(x) \) is not known and should be found from quantum chemical calculations. In terms of our model, \( V \) is assumed to depend on the \( x \) coordinate only because the displacement along this coordinate is more significant during diffusion hop than along the \( z \) coordinate. We use an empirical form for \( V(x) \),

\[
V(x) = V_0 \exp[-(x - \Delta x_0/2)^2/l_x^2] \quad (15)
\]

where \( \Delta x_0 = x_{at} - x_0 \), and \( l_x \) is the characteristic length, which usually is taken\(^19 \) to be 1 Å. Equation 15 gives the correct qualitative behavior of the dependence of \( V \) on \( x \). It has a Gaussian shape with a local maximum at \( \Delta x_0/2 \). Although this approach does not have a rigorous quantum chemical basis, it should provide a plausible initial step for interpolation between two diabatic PESs.

3. Transition Probability for the Diffusion Step

The standard semiclassical transition state theory expression for the hopping frequency on the adiabatic PES is given by eq \( 16,3 \)

\[
W(j, k) = \frac{k_B T}{h} \left( \frac{Z_j}{Z_k} \right) \exp[-E_{\text{diff}}^j(j, k)/k_B T] \quad (16)
\]

where \( Z_j \) is the partition function per unit length for the initial state; \( Z_k \) is the incomplete partition function per unit length for the transition state, the degree of freedom corresponding to the reaction coordinate being omitted; and \( E_{\text{diff}}^j \) is the activation energy for the \( j \rightarrow k \) diffusion transition.

In terms of the described model, we determine the diffusion activation energy of a partial transition as the difference between the values of the potential energies on the adiabatic PES (eq 14) at the saddle point and at the initial state. The saddle point coordinates are calculated by following the technique previously developed for other processes.\(^{19,20,23} \) For the considered system we obtain, using this method, three equations determining the saddle point coordinates \((\xi, \xi, \theta)\),

\[
U_j(x, z, \theta) - U_i(x, z, \theta) = \frac{V(\theta)(2\theta - 1)}{\sqrt{(\theta)(1 - \theta)}} \quad (17)
\]

\[
(1 - \theta) \left\{ \frac{\partial U_i(x, z, \theta)}{\partial x} + \theta \left[ \frac{\partial U_i(x, z, \theta)}{\partial x} \right] \right\} = \frac{2}{\sqrt{(\theta)(1 - \theta)}} \left\{ \frac{\partial V(\theta)}{\partial x} \right\} \quad (18)
\]

\[
(1 - \theta) \left\{ \frac{\partial U_i(x, z, \theta)}{\partial z} + \theta \left[ \frac{\partial U_i(x, z, \theta)}{\partial z} \right] \right\} = 0 \quad (19)
\]

where \( \theta \) is the same quantity as that in eqs 12–13.

The activation barrier for diffusion is determined from the saddle point coordinates when substituted into eq 14. Because the origin of coordinates is at the zero point of the initial PES (see eq 10), we have eq 20.

\[
E_{\text{diff}} = U(\xi, \xi, \theta) \quad (20)
\]

Equation 20 may be transformed\(^{19,20} \) to the form eq 21.

\[
E_{\text{diff}} = U(\xi, \xi, \theta) - \frac{V(\xi)}{\sqrt{(1 - \theta)^3/\theta}} = u(\xi) + v(\xi) + \tilde{\omega}_j T - \frac{V(\xi)}{\sqrt{(1 - \theta)^3/\theta}} \quad (21)
\]

Let us consider the partition functions in eq 16. The partition function at the initial state (i) is equal to \( Z_i = Z_x Z_y Z_\theta \), where \( Z_x, Z_y, \) and \( Z_\theta \) are the partition functions for vibrational motion in the \( u_i(x), v_i(z) \), and \( w_i(\theta) \) potentials, respectively. These partition functions are easily calculated in the model of harmonic oscillators,

\[
Z_n = 1/[1 - \exp(-\hbar \omega_n/k_B T)] \quad (22)
\]

where \( n \) is \( x, y, \) or \( \theta \). To calculate \( Z_\theta \), we approximate the APES\(^14 \) near the saddle point by the following expansion,

\[
U = U + \frac{1}{2} \sum_{n=1}^{3} \chi_{nm}(s_n - \xi_n)(s_m - \xi_m) \quad (23)
\]

where \( s_{nm} \) are the mass-weighted coordinates corresponding to coordinates \( x, y, \) and \( \theta \), and \( \chi_{nm} \) and \( \hat{U} \) are the second derivatives and the value of \( U \) at the saddle point, respectively. The eigenvalues of the matrix equation (eq 24),

\[
|\delta_{nm} - \chi_{nm}| = 0 \quad (24)
\]

where \( \delta_{nm} \) is the Kronecker symbol, gives three frequencies \( \omega_i \) \((i = 1, 2, \) and \( 3) \) characterizing the transition state; one of them has an imaginary value \( i\omega_1 \), whereas two others \( \omega_2 \) and \( \omega_3 \) are real. Therefore, finally, we rewrite eq 16 in the following form,

\[
W(j, k) = \frac{k_B T}{h} \frac{Z_2 Z_3}{Z_1 Z_2 Z_3} \exp[-E_{\text{diff}}(j, k)/k_B T] \quad (25)
\]

where \( Z_2 \) and \( Z_3 \) are the partition function for the transition state, which correspond to the frequencies \( \omega_2 \) and \( \omega_3 \). Now, using eq 25 we can calculate the terms of eqs 7–9 and, therefore, estimate the coefficients for different types of the surface diffusion.

4. Model Potentials

To represent eqs 17–19 in an explicit form we have to approximate the components \( u_i(x) \) and \( u_i(x) \) of the PES by appropriate functions. Because these PESs do not account for the interaction with the neighboring adsorption sites, the potential wells, in which adsorbed particles are trapped, are symmetric with respect to the position of the corresponding
adsorption site. It is clear that the interaction of a particle with the adsorption site decreases with the increasing distance between them. One of the simplest semiempirical ways to describe this interaction is to use the “attractive” branch of the Morse curve. Therefore, we shall present the \( u_i(x) \) and \( u_f(x) \) as follows,

\[
  u_i(x) = D_i \left[ 1 - \exp \left( -\alpha_i x \right) \right]^2 \tag{26}
\]

\[
  u_f(x) = D_f \left[ 1 - \exp \left( \alpha_f (x - \Delta x_0) \right) \right]^2 \tag{27}
\]

where \( 0 < x < \Delta x_0 \) (Figure 3). In eqs 26 and 27, \( D_i \) and \( D_f \) are the depths of the potential well, which we associate with the corresponding absolute values of the adsorption energies characterizing both the specific site (on-top, bridge, or hollow) and the specific adsparticle; \( \alpha_i \) are the anharmonicity parameters equal to \( \alpha_i = \omega_{i0} \sqrt{\mu / 2D_{i0}} \) where \( \mu \) is the corresponding reduced mass, which may approximately be taken to be the mass of the adsorbed particle; \( \Delta x_0 \) is the distance between the initial and final adsorption sites; and \( \omega_{i0} \) is the frustrated vibration frequency in the initial and final potential wells.

Unlike the potentials \( u_i(x) \) and \( u_f(x) \), the potentials \( v_i(z) \) and \( v_f(z) \) are nonsymmetric and have a repulsive character when the distance between the particle and metal surface decreases with respect to the equilibrium one. Therefore, they will be approximated by the full Morse functions having both attractive and repulsive branches (Figure 4).

\[
  v_i(z) = B_i \left[ 1 - \exp \left( -\beta_i \left( z - z_{0i} \right) \right) \right]^2 \tag{28}
\]

\[
  v_f(z) = B_f \left[ 1 - \exp \left( -\beta_f \left( z - z_{0f} \right) \right) \right]^2 \tag{29}
\]

Substitution of eqs 15 and 26–29 into eqs 17–19 leads to eqs B1–B3, given in Appendix B, which are used for numerical calculations of the saddle point coordinates.

5. Numerical Estimations of the CO Diffusion Coefficients

We apply the approach presented above to the calculations of the diffusivity of CO molecules adsorbed on (111) surfaces of ruthenium, rhodium, palladium, iridium, and platinum. To perform these calculations we need the values of the adsorption energies \( E_{ads} \), adsorption heights \( z \), and adsorption frequencies \( \omega \) characterizing CO adsorption on different sites of these metal surfaces. The values of \( x \) coordinate are determined by the geometrical structure of the (111) metal surface.

5.1. Parameters. In principle, one could extract all of these parameters either from published quantum chemical studies of CO adsorption on the metals or from experimental data. The difficulty, however, stems from the fact that although the frequencies and adsorption heights (i.e., the equilibrium distances between the adsorbed particle and the metal surface) depend only weakly on the computation methods or experimental techniques, the adsorption energies for the same site vary considerably with the computation method; furthermore, there is no published work where the whole set of required parameters was calculated or measured in the framework of the same approach. Thus, in this paper we use the CO adsorption characteristics calculated by us elsewhere, which are listed in Table 1. In addition to these data, Table 1 also includes characteristics of the CO bridge adsorbed state. They were extracted from published works. The following comments are in order. The calculations of the hollow adsorption energy for platinum and calculations of the bridge energy for platinum and ruthenium lead to the values that do not agree with the experimental site preference. However, the calculations of the CO corrugation potential for other metals give the correct sequence of the on-top, bridge, and hollow adsorption energies.

Regarding the CO adsorption on (111) Pt, many theoretical and experimental papers were devoted to studying the corresponding corrugation potential. Experimental works show that the energy of the bridge adsorbed state on platinum is lower than the energy of the on-top state (usually by \( \sim 0.6 \) to 1.5 kcal/mol) and this energy may be taken to be equal to the energy of the hollow adsorbed state. Some theoretical works lead to similar results whereas others point to other preferred sites and energies (the so-called Pt(111) puzzle). Due to the problem with localization of the CO bridge adsorbed state on the potential energy surfaces of platinum (and ruthenium as well), we estimated the energies of the bridge state using the on-top and the hollow adsorption energies calculated in ref 24 and the differences between the energies of the on-top and bridge states taken from the above referred published works. To be consistent, we used the same approach for the estimation of the bridge adsorbed energies of CO on other metals; in the case of palladium, the on-top energy was substituted by the hollow one.

Table 1 does not include the frequency of surface frustrated vibrations of CO. This frequency was measured in ref 45 where the studying CO adsorption on (111) platinum surface was performed. The reported value is in the range of \( \sim 50 \) to 60 cm\(^{-1}\). Theoretical estimation of the frequency in the harmonic ap-

![Figure 3](image)

**Figure 3.** Morse potential energy curves, \( u_i \) and \( u_f \), along \( x \) coordinate connecting \( h \)- and \( b \)- adsorption sites on a surface; solid lines denote the “attractive” branches describing the interaction of a particle with the adsorption site; \( a \) is the metal–metal distance, \( \Delta x_0 \) is the difference of the \( x \) coordinates corresponding to the two energy minima; \( 2V_0 \) is the energy gap.

![Figure 4](image)

**Figure 4.** Morse potential energy curves, \( v_i \) and \( v_f \), along \( z \) coordinate perpendicular to a surface; \( \Delta z_0 \) is the difference of the \( z \) coordinates corresponding to initial and final potential energies.
proximation results in a value of 20–100 cm$^{-1}$. In our diffusion calculations this frequency was taken to be equal to 60 cm$^{-1}$ for all metals. To estimate the reorganization parameter ($E_r$) the frequency of metal–metal vibrations was taken to be equal to $k_B T/h \approx 200$ cm$^{-1}$ at 300 K, and change of the metal–metal bond lengths near an adsorbed CO molecule was taken to be equal to 0.05 Å. For twelve neighboring bonds these values of the frequency and $\Delta r$ lead to $E_r \approx 6$ kcal/mol. The similar values of $E_r$ were estimated for other surface processes.$^{19,23}$ The energy gap ($2V_0$) at the crossing point of the diabatic PESs ($U_t$ and $U_b$) was taken to be equal to 6 kcal/mol.$^{19}$ We studied for CO diffusion on rhodium the sensitivity of the activation energy to changes in $E_r$ and $V_0$ and found $E^\text{diff}_a = 6.3$ kcal/mol for $E_r$, $V_0 = (6, 3$ kcal/mol), $E^\text{diff}_a = 6.6$ kcal/mol for $(4, 2)$, $E^\text{diff}_a = 5.8$ kcal/mol for $(4, 3)$, and $E^\text{diff}_a = 6$ kcal/mol for $(5, 3)$. Equilibrium metal–metal distances ($a$) were calculated$^{24}$ by geometry optimization on bare 98/7 and 6/6/5 clusters and were taken as average values for both structures (see Table 1).

5.2. Results. Using parameters listed in Table 1 we calculated both the saddle point coordinates on the potential energy surfaces for five cluster/C0 systems (eqs 17–19) and the frequencies characterizing the corresponding transition states (eq 24). One imaginary value that describes moving the system along the reaction coordinate over 3D PES and two real frequencies were found. Specifically, for CO diffusion on rhodium surface, these frequency sets were found to be equal to 352i, 81, and 21 cm$^{-1}$ ($t \rightarrow b$ hopping) and 345i, 81, and 39 cm$^{-1}$ ($t \rightarrow h$ hopping). In the case of iridium, platinum, and ruthenium, the values of the imaginary frequency at the transition state for $t \rightarrow b$ and $t \rightarrow h$ hopping were found to be equal to 341i and 233i; 532i and 698i; and 203i and 2121 cm$^{-1}$, respectively. The imaginary frequencies at the transition states for $h \rightarrow b$ and $h \rightarrow t$ hopping on palladium surface were found to be equal to 113i and 226i cm$^{-1}$. All the imaginary frequencies may be considered as classical, which allows us to apply the theory of rate processes for calculating the pre-exponential factor of diffusion by hopping.

The calculated values of CO diffusion coefficients ($D$ [cm$^2$/s]), the activation energies ($E^\text{diff}_a$), and the pre-exponents ($D^\text{diff}_a$) (Table 1) show good agreement with the corresponding available experimental values on Ru and Rh. Experimental activation energies for platinum measured in refs 16–18 are strongly scattered, and our value of $E^\text{diff}_a$ falls within this interval of the values. We did not find experimental data for ruthenium and iridium.

The activation energy is the lowest for palladium and is the highest for iridium. We note that, in contrast to other considered metals, the preferable site for CO adsorption on palladium is the hollow one (Table 1), and CO may diffuse along the palladium surface by the $h$-$t$-$h$ and the $h$-$b$-$h$ mechanisms (see Figure 2). The latter diffusion mechanism is more favorable as it is characterized by a lower activation barrier (2 kcal/mol) for the $h$-$b$ partial transition than the former, for which the $h$-$t$ partial hopping is characterized by an activation energy equal to 14.5 kcal/mol; both contributions lead to the effective activation barrier of $\approx 2.2$ kcal/mol. As follows from our calculations, CO diffusion on ruthenium proceeds by the two mechanisms $t$-$h$-$t$ and $t$-$b$-$t$ with approximately equal probabilities and diffusion on rhodium; platinum and iridium proceed mainly by the $t$-$b$-$t$ path.

Let us compare the diffusion activation barriers calculated in terms of our approach with those calculated under a priori assumption that the bridge adsorbed state is the transition state for the $t$- and the $h$-diffusion.$^{12–14}$ In that model, $E^\text{diff}_a = E_{\text{ads}}^\text{bridge} - E_{\text{ads}}^\text{top}$ for all metals except palladium, for which $E^\text{diff}_a = E_{\text{ads}}^\text{bridge} - E_{\text{ads}}^\text{hollow}$. Using the adsorption energies listed in Table 1 we calculate the corresponding activation barriers for Ru, Rh, Ir, and Pt to be equal to 3.4, 3.8, 4.5, and 1.5 kcal/mol, respectively. For palladium, the activation barrier is calculated to be equal to 1 kcal/mol. These values, which are given in Table 1 in square brackets, are significantly lower than those calculated with the use of our approach and are also lower than published experimental data. Therefore, this result does not support the above-mentioned assumption of authors.$^{12–14}$ One can see from Table 1 and Figure 5 that the value of $E^\text{diff}_a / E_{\text{ads}}$ is equal to $\approx 0.2$ for these metals except for palladium (0.06). This result is not surprising because CO diffusion on palladium is characterized by a different diffusion mechanism.

Conclusions

A simple analytical SP-SE-APES model was developed to calculate the diffusion coefficients of an adsorbed particle on a metal surface. The adsorption characteristics of this particle determine the form of the APES when moving along the metal surface. We apply it to study CO diffusion on the surfaces of five transition metals. Calculated diffusion coefficients and their temperature dependencies are in good agreement with experimental data. Various diffusion mechanisms are analyzed: CO diffusion on a palladium surface was found to proceed mainly by hopping from the $h$- through the $b$-site to the $h$-sites, whereas on rhodium, iridium, and platinum it proceeds mainly by hopping from the $t$- through the $b$-site and to the $t$-sites; two mechanisms ($t$-$b$-$t$ and $t$-$h$-$t$) are realized with approximately equal probabilities when CO diffuses over ruthenium. The activation barrier for CO diffusion is about 0.2 of the heat of CO desorption. Room-temperature diffusivity is $10^{-6}$ cm$^2$/s in order of magnitude, except for Pd where it is 2 orders of magnitude higher.

Appendix

A

Equation 1 of the main text for the $h \rightarrow b \rightarrow h$ diffusion mechanism is obtained as follows. Particle A, initially adsorbed on the $0_0$ site (Figure 2), may diffuse to one of the neighboring three $0_0$-sites or to one of the neighboring three $0_0$-sites. The probability of hopping of A from the $0_0$ to a $0_0$ ($i = 1, 2,$ and 3), for example to the $0_1$ is equal to $(1/6)W(0_0, 0_1)$ where 1/6 is the weight factor. Then, the particle A being on the $0_0$ site has four possibilities: to come back to $0_0$, to fall into $1_1$, or to hop to one of two neighboring $0_0$-sites, $0_0$ or $0_0$. Therefore, the probability of the $0_0 \rightarrow 1_1$ transition is equal to $(1/4)W(0_0, 1_1)$, and the probability of the sequential $0_0 \rightarrow 0_1 \rightarrow 1_1$ transition is equal to
Using similar arguments, we can calculate the probabilities \( W_2 \) and \( W_3 \) of hopping the A particle from the \( h_0 \) site to each of two neighboring \( h_i \)-sites through the \( h \rightarrow b \rightarrow h \) mechanism. Obviously, all these probabilities are equal to each other, and they describe the hopping of the A particle by the minimal distance between the \( h \) sites equal to \( \lambda_1 = \lambda_2 = \lambda_3 = \lambda = a/\sqrt{3} \). Then, calculating the sum \( \sum_{i=1}^{5} \lambda_i^2 W_i = 3 \lambda^2 W \), we obtain the expression for the diffusion coefficient \( D_{hh} \) via the \( h \rightarrow b \rightarrow h \) mechanism given by eq 5 of the main text.

Next, let us consider the diffusion of an adsorbed particle through the \( h \rightarrow t \rightarrow h \) mechanism. Because the weight factor for the diffusion of a particle A from the \( t \) site to a neighboring site \( t \) \((k = 0, 1, 2)\) is equal to \( 1/6 \) (see text above), the probability of this transition is equal to \((1/6)W(0, t, 0)\). The particle A being on a \( t \) site, for example, on the \( t_0 \) site, has six possibilities to hop to a neighboring \( h_i \)-site \((i = 0, 1, 5)\), and it has six possibilities to hop to a neighbor \( h_0 \)-site \((b_01, b_02, b_06)\), see Figure 2. Therefore, the weight factor of a \( t_k \rightarrow h \) transition is equal to \( 1/12 \), and the probability of the \( h_0 \rightarrow t_0 \rightarrow h_1 \) transition may be written as eq A2

\[
W(001) = \frac{(1/6)W(0, 0, 0)(1/12)W(t, 0, h_1)}{(1/6)W(0, t, 0) + (1/12)W(t, 0, h_1)} \quad (A2)
\]

Although all probabilities \( W(0, k) \) are equal to each other, the corresponding minimal distances between \( h \)-sites for five \( h_0 \rightarrow t_0 \rightarrow h_1 \) transitions are different: \( \lambda_{01} = \lambda_{03} = a/\sqrt{3}, \lambda_{03} = \lambda_{04} = a_0 \), and \( \lambda_{04} = 2a/\sqrt{3} \). By summing these probabilities multiplied by the corresponding squared lambda we have eq A3

\[
D_{h_{hh}} = \sum_{k=1}^{5} \lambda_{0k}^2 W(0k) = \frac{1}{12}W(0, 0, t) + 6W(0, 0, h_1) = \frac{3}{12W(0, 0, t) + 6W(0, 0, h_1)} [2(\lambda_{01})^2 + 2(\lambda_{03})^2 + (\lambda_{04})^2] = 12\lambda^2 \frac{W(0, t, 0)W(0, h_1)}{2W(0, 0, t) + W(0, 0, h_1)} \quad (A3)
\]

**B**

Equations 13–15 may be rewritten in an explicit form using the specific expressions for the diabatic potentials giving by eqs 22–25:

\[
D_1[1 - \exp(-\alpha x)]^2 - D_2[1 - \exp(\alpha(x - \Delta x))]^2 + B_1[1 - \exp(-\beta z)]^2 - B_2[1 - \exp(-\beta(z - \Delta z))]^2 - \frac{1}{2} \Delta E = \frac{V(2\theta - 1)}{\sqrt{\theta(1 - \theta)}} \quad (B1)
\]

\[
D_1 \alpha(1 - \theta)\exp(-\alpha_x - \exp(-2\alpha x)) - D_1 \alpha \theta \exp(\alpha x - \Delta x) - \exp(2\alpha x - \Delta x) = (dV/dx)\sqrt{\theta(1 - \theta)} \quad (B2)
\]

\[
B_1 \beta(1 - \theta)\exp(-\beta z) - B_2[1 - \exp(-\beta(z - \Delta z))] - \exp(-2\beta z) = 0 \quad (B3)
\]

where \( V \) is given by eq 11, and \( x_0 \) and \( z_0 \) were taken to be equal to zero, \( x_0 = \Delta x = x_0 = 0, z_0 = \Delta z = z_0 = 0 \).