Theory of Dissociative Adsorption Kinetics of Homonuclear Diatomic Molecules on Solid Surfaces

Ernst D. German,[*,†] **Irena Efremenko,**[†] **Alexander M. Kuznetsov,**[‡] **and Moshe Sheintuch**[†]

Department of Chemical Engineering, Technion - Israel Institute of Technology, Haifa 32000, Israel, and Institute of Electrochemistry of the Russian Academy of Sciences, Leninsky Prospect 31, 117071 Moscow, Russia

Nonadiabatic theory of chemical reactions is applied to the kinetics of the dissociative adsorption of homonuclear diatomic molecules on transition metal surfaces. Coordinates that characterize substrate nuclei vibrations are introduced into the theoretical model to take into account a reorganization of the substrate structure under adsorption process along with those that characterize approaching of an adsorbate molecule X_2 to a substrate S and vibration motion of the molecule. The substrate is modeled by a set of the classical harmonic oscillators. An approximate expression for the activation energy is obtained under general assumptions about the form of both intermolecular potentials v_i and v_f characterizing the interaction of the adsorbate and substrate, and intramolecular potentials u_i and u_f characterizing the interaction between X atoms in the initial and final states, respectively. These assumptions allow one to calculate the activation energy in the explicit form without the detailed information about these interaction potentials. In the model, the activation energy to the dissociation is determined by the repulsive interaction of reactants, the substrate reorganization energy, and an effective energy of the reaction.

1. Introduction

Interaction of diatomic molecules such as H_2, O_2, and N_2 (in general, X_2) with transition metal surfaces has been studied widely by experimental and theoretical methods for various catalytic processes of commercial importance. As a result of numerous investigations (see reviews 1–7 and references herein), several common and specific details of such interactions that lead to the formation of different adsorptive states of X_2 on the surface of substrate S were established. Three main types of surface states were identified. At long distances between an incoming molecule X_2 and a substrate S, typically ∼2.5–3.5 Å, weakly bounded (physisorbed) states are formed. In these states, the X_2 molecule is only slightly excited as compared to its gas-phase state. The potential well for the physical adsorption is usually not deep, about a few kilocalories per mole. For example, physically adsorbed states were experimentally identified at low temperatures for O_2 adsorption on platinum[8–10] and for H_2 adsorption on copper[11] and on silver.[12] At X_2–S distances on the order of chemical bonds (∼1.4–1.9 Å), one or several molecular chemisorbed states, in which the X_2 molecule is notably excited with respect to its isolated state, are formed. A different charge transfer between substrate and X_2 molecule distinguishes these chemisorbed states. For example, at least four molecular chemisorbed states of O_2 molecule were found experimentally on some metal surfaces.[8–10,13,14] The transformation of the physisorbed state into the chemisorbed one usually is an activated process. Further approach of X_2 molecule to a substrate leads to its dissociation into X atoms with formation of strong S–X surface bonds (dissociative or atomic adsorption).

While the elementary stage of dissociation of molecularly adsorbed X_2 molecule always requires overcoming of an activation barrier, effectively the total reaction $X_2^{gas} \rightarrow 2X^{ads}$ could proceed as a nonactivated or as activated process.[15,16] For instance, dissociative hydrogen adsorption on platinum and palladium proceeds, according to the experimental data,[17,18] as the nonactivated process, while the dissociative adsorption of oxygen on these metals is characterized by notable effective activation energy.[10,19–21]

Therefore, generally speaking, the potential energy surface (PES) for the dissociative adsorption of X_2 molecule on metal surfaces is characterized by three areas of the stationary states, as presented schematically in Figure 1 by one-dimensional PES cross section along the minimal energy reaction pathway for a system X_2/S. So, the detailed analysis of the total potential surface is needed for accurately calculating the adsorption kinetics of the X_2/S system.

Dissociation of an admolecule and coincident formation of the adsorbate–substrate bonds present a key elementary step in chemisorption and catalysis. The height of an activation barrier to the X_2 dissociation eventually determines the kinetics of chemisorption and the state of an adsorbate on a particular surface at given conditions. Understanding the origin of reaction barriers presents the first step toward catalyst design.

With the development of the density functional theory and with large increase of computer power, quantitative theoretical determination of the adsorption heat of different atoms and molecules on transition metal surfaces becomes possible. However, the calculation of the total potential surface appears to be a significantly more complicated task, mainly because of the existence of numerous nearly degenerated electronic terms in the transition metal systems. Thus, approximate estimation of the activation barriers still is often applied for such systems. Several approximations were developed to describe the activa-

---

* To whom correspondence should be addressed. E-mail: cermsge@tx.technion.ac.il. Fax: 972-4-8230476.
† Technion - Israel Institute of Technology.
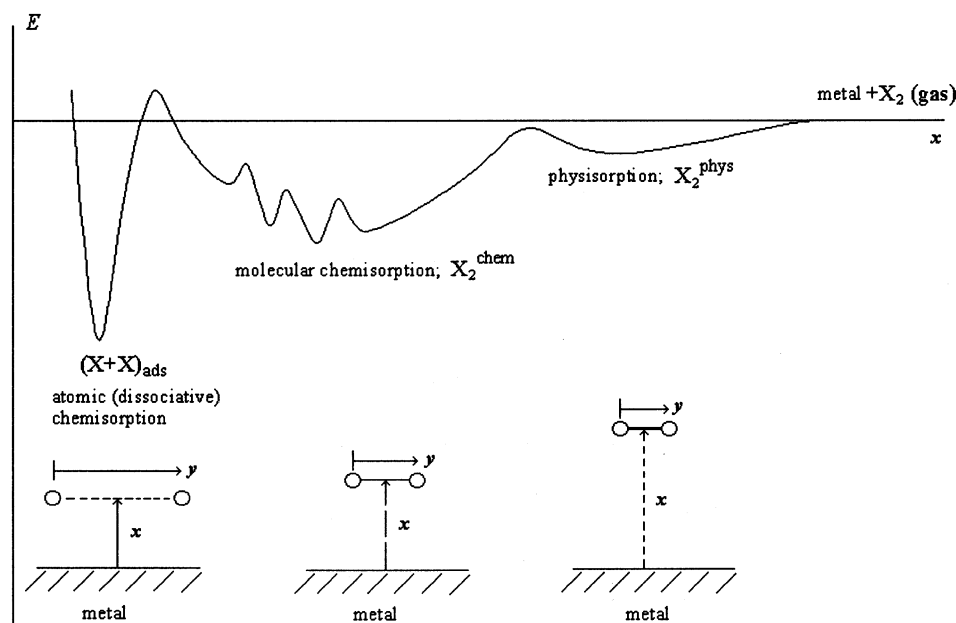‡ Institute of Electrochemistry of the Russian Academy of Sciences.

Theory of Dissociative Adsorption Kinetics

J. Phys. Chem. B, Vol. 106, No. 45, 2002 **11785**

Figure 1. Adsorption states of a molecule X_2 on a metal M. x and y are the coordinates describing intramolecular vibrations of X_2 and intermolecular vibrations of that relatively of the substrate, respectively.

tion energies for the chemisorption.[22-26] The phenomenological approach bond-order conservation Morse potential (BOC-MP)[25] or its improved version the unity bond index−quadratic exponential potential (UBI-QEP)[26] is the simplest and most widely used out of them (see, for example, refs 27−33). In this formalism, the barrier E_a to the dissociative adsorption and the heat of the reaction $X_2^{ads} \rightarrow 2X^{ads}$ on a surface, ΔE_{surf}, are connected by the relationship

$$E_a = {}^1/_2(\Delta E_{surf} + Q_x/2) \qquad (1)$$

where Q_x is the adsorption energy of X atom on surface S. Thus, the BOC-MP/UBI-QEP scheme takes into account only two stationary states on the PES, the initial physisorbed and the final dissociated states. For some reactions, such an approach provides the heats of adsorption and reaction activation barriers with the reasonable accuracy of 1−3 kcal/mol.[3] For others, the estimated values differ more significantly from those measured experimentally or calculated by high-level quantum chemical methods. In these cases, it was suggested[33] to apply a specific linear scaling constant to each particular system to get better agreement with experiment.

In the present work, a new model for the description of the dissociative X_2 adsorption on a metal surface is suggested, and it is capable of interpreting the physical ground of the activation barrier to the dissociative adsorption of a diatomic molecule X_2 on a substrate. The model is based on the concept of the nonadiabatic chemical reaction kinetics theory developed in refs 34−37. This model could be applied for the calculation of the transition probability between different adsorption states.

Analysis of the literature data[3,38] and our previous result[39] led us to the conclusion that the chemisorption process may be accompanied by a structural reorganization of solid surface. This means that coordinates characterizing molecular vibrations of substrate in addition to coordinates of adsorbate molecule X_2 must be introduced into the theoretical model. In our theory, we consider the individual contributions into the activation energy owing to three main components, repulsive interaction between nondissociated X_2 molecule and substrate surface, substrate metal−metal bond relaxation, and the reaction heat.

Besides, the employed approach allows us to analyze the preexponential factor and, therefore, to get the analytic expression for dissociative adsorption kinetics.

The remainder of the paper is organized as follows. In section 2, a theoretical model is formulated. Calculation of the rate constant of chemisorption process is performed in section 3. In section 4, an approximate expression for E_a is given. Numerical estimations are given in the section 5. The paper is ended by short conclusions.

2. Model

In this section, we outline the theoretical model used in our calculations. Throughout this paper, we assume the molecule X_2 to be in a position parallel to a surface; perpendicular rotations are not taken into account (see Figure 1). This arrangement of X_2 relative to substrate surface is according to results of electron structure calculations.[40,41] It was shown in these works that cartwheel rotations of the molecular axis out of the favorable orientation parallel to the surface are connected with a large increase of the potential energy. Helicopter rotations, on the other hand, are hindered mainly because of steric restrictions if the Pd−H distance becomes shorter than a typical Pd−H bonding length. The initial, U_i, and final, U_f, potential surfaces are introduced to describe an *elementary reaction step* of the dissociative adsorption of a X_2 molecule on a substrate S. The transition of a weakly interacting (physisorbed) state of X_2 to a molecular (or atomic) chemisorbed state (according to the notation in Figure 1) or the transition between two chemisorbed states may serve as an example of this step. Each of these potential surfaces represents the total energy of the whole system that depends on a set of coordinates $\{q_\alpha\}$ describing the vibrations of the substrate nuclei, on the distance x between the center of mass of X_2 and the surface S, and on the coordinate y describing the intramolecular vibrations of X_2 molecule. The symbol X_2 is used here as a general notation of the reactant in the undissociated and dissociated state.

The simplest form of U_i and U_f corresponds to surfaces under the assumption that the interaction between vibration modes along the coordinates x, y, and $\{q_\alpha\}$ is absent. In this case, both potential surfaces may be written as a sum of three separate

11786 *J. Phys. Chem. B, Vol. 106, No. 45, 2002*

German et al.

contributions. One of them is due to the potential $v(x)$ that characterizes the interaction between X_2 and S in the direction perpendicular to the surface. The second contribution is due to vibrational potential $u(y)$ for X_2, and the third term, $u_s(\{q_\alpha\})$, is due to the vibrations of the substrate nuclei, which are supposed to be classical. Thus, providing these components with the indexes "i" and "f" for the initial and final state, respectively, we have

$$U_i(x,y,\{q_\alpha^i\}) = u_s^i(\{q_\alpha^i\}) + u_i(y) + v_i(x) + I_i \quad (2')$$

$$U_f(x,y,\{q_\alpha^f\}) = u_s^f(\{q_\alpha^f\}) + u_f(y) + v_f(x) + I_f \quad (2'')$$

where I_i and I_f are the minimum values of the potential energies in equilibrium states that include electron energies. Consideration of the effect of motion along the coordinate x on equilibrium values of the coordinates y and $\{q_\alpha\}$ is not of the principal difficulties. It can be made, for example, in the linear approximation with the approach developed in ref 35. In our theory, we restrict ourselves to simpler analysis.

Let us use the harmonic approximation to describe vibrations of the substrate atoms, which are supposed to be small. In this model, functions u_s^i and u_s^f could be represented as sums of the harmonic potentials of a set of independent oscillators, that is,

$$u_s^i = \frac{1}{2}\sum_\alpha \hbar\omega_\alpha^i (q_\alpha^i - q_{\alpha 0i}^i)^2 \quad (3')$$

$$u_s^f = \frac{1}{2}\sum_\alpha \hbar\omega_\alpha^f (q_\alpha^f - q_{\alpha 0f}^f)^2 \quad (3'')$$

where $q_{\alpha 0i}^i$ and $q_{\alpha 0f}^f$ are the equilibrium values of normal coordinates q_α^i and q_α^f, ω_α^i and ω_α^f are the corresponding vibration frequencies of an oscillator α. The dimensionless coordinates $q_\alpha^{i(f)}$ are expressed through the Cartesian coordinates s_α as follows

$$q_\alpha^{i(f)} = \sqrt{\frac{m\omega_\alpha^{i(f)}}{\hbar}}s_\alpha$$

where m is the effective mass of the oscillator and are related by

$$q_\alpha^f = (\omega_\alpha^f/\omega_\alpha^i)^{1/2}q_\alpha^i$$

Vibrational energies of the oscillator α in the potential wells u_s^i and u_s^f are equal to

$$\epsilon_{s,n_\alpha}^{i(f)} = \hbar\omega_\alpha^{i(f)}\left(n_\alpha + \frac{1}{2}\right) \quad (4)$$

The analytical forms of the potentials $u_{i(f)}$ and $v_{i(f)}$ are not specified at this point and will be discussed later.

3. Rate Constant

The final goal of calculations is to determine the average probability of transition per unit time (rate constant) from the initial potential energy surface U_i (eq 2') to the final potential energy surface U_f (eq 2''). The most appropriate method for

nonadiabatic reactions is the Fermi Golden Rule.[34,42] Thus, we shall represent the transition probability in the form

$$W = \frac{1}{Z_x Z_y}\int dx\, \exp\left[-\frac{v_i(x)}{k_BT}\right]\int dy\, \exp\left[-\frac{u_i(y)}{k_BT}\right]w(x,y) \quad (5)$$

where

$$w(x,y) = \frac{2\pi}{\hbar}Z_s^{-1}\sum_{i,f} e^{-(E_i/(k_BT))}\,|\langle\Psi_f|V^i|\Psi_i\rangle|^2\,\delta(E_i - E_f) \quad (6)$$

In eq 5, Z_x is the configurational integral for the x-mode in the initial state and Z_y is the same for the y-mode, and in eq 6, Z_s is the vibrational statistical sum for substrate in the initial state equal to the product of vibrational statistical sums for $\{\alpha\}$ oscillators. Ψ_i, Ψ_f and E_i, $E_{f\sim}$ are the total wave functions and energies of the initial and final states, and subscripts i and f involve all quantum numbers of initial and final states, respectively. V^i is the perturbation interaction leading to the reaction. This perturbation presents the attractive interaction of a X_2 molecule with a substrate in the case of a bulk metal surface. It may be the spin−orbit coupling if the initial and final states of the system have different multiplicity as in the case of triplet−singlet transition characterizing the dissociative reaction on small palladium clusters.[41] The corner brackets denote the integration over all coordinates. The Dirac delta function describes the energy conservation law. It imposes a constraint on the summation over the initial and final states, allowing only the terms that correspond to equal energies. Equation 6 determines the probability of the transition at fixed values of the coordinates x and y. The total probability given by eq 5 is obtained by the weighted integration of eq 6 over x and y.

Application of the Born−Oppenheimer approximation[36] for the separation of the electronic and nuclear motions leads to the following approximate representation of the total wave functions

$$\Psi_i = \varphi_i(\{r_k\},\{q_\alpha^i\},x,y)\chi_{\{n_\alpha\}}^i(\{q_\alpha^i\}) \quad (7')$$

$$\Psi_f = \varphi_f(\{r_k\},\{q_\alpha^f\},x,y)\chi_{\{k_\alpha\}}^f(\{q_\alpha^f\}) \quad (7'')$$

where φ_i and φ_f are the electron wave functions and $\chi_{\{n_\alpha\}}^i$ and $\chi_{\{k_\alpha\}}^f$ and are the vibrational wave functions of the substrate nuclei. The electron wave functions depend, in general, on nuclear coordinates x, y, and $\{q_\alpha\}$. Then, the electron matrix element, (V_{fi}^i), which is obtained after integration in eq 6 over the electronic coordinates $\{r_k\}$, also depends on the nuclear coordinates $\{q_\alpha\}$, y, and x. The simplest and rather general results are obtained when this dependence may be neglected (Condon approximation[34]). The electron matrix element may therefore be taken out of the sum

$$W = \frac{2\pi|V_{fi}^i|^2}{\hbar Z_s Z_x Z_y}\int dx\, e^{-v_i(x)/(k_BT)}\int dy\, e^{-u_i(x)/(k_BT)} \times$$

$$\sum_{\{n_\alpha\},\{k_\alpha\}} e^{-\epsilon_{s,n\alpha}^i/(k_BT)}|\langle\chi_{k_\alpha}^f||\chi_{n_\alpha}^i\rangle|^2\,\delta(E_{n_\alpha}^i - E_{k_\alpha}^f) \quad (8)$$

where the summation is performed now only over vibrational states $\{n_\alpha\}$ and $\{k_\alpha\}$ and the sum normalized by the partition function of the initial state represents the averaged nuclear Franck−Condon factor.

Theory of Dissociative Adsorption Kinetics

J. Phys. Chem. B, Vol. 106, No. 45, 2002 **11787**

The delta function may be expressed in the integral form

$$\delta(E^i_{n_\alpha} - E^f_{k_\alpha}) = \frac{1}{2\pi i k_B T}\int_{c-i\infty}^{c+i\infty} d\theta \times$$

$$\exp\left[-\frac{\theta(\Delta I + \sum_\alpha \epsilon^f_{s,k_\alpha} - \sum_\alpha \epsilon^i_{s,n_\alpha} + v_f(x) - v_i(x) + u_f(y) - u_i(y))}{k_B T}\right]$$

(9)

where $\Delta I = I_f - I_i$. Substituting eq 9 into eq 8 and taking into account eq 4, we obtain eq 10

$$W = \frac{|V^i_{fi}|^2}{i\hbar k_B T Z_s Z_x Z_y}\int_{c-i\infty}^{c+i\infty} d\theta \exp\left(-\frac{\theta \Delta E}{k_B T}\right)\int dx \times$$

$$\exp\left[-\frac{(1-\theta)v_i(x) + \theta v_f(x)}{k_B T}\right]\int dy \times$$

$$\exp\left[-\frac{(1-\theta)u_i(y) + \theta u_f(y)}{k_B T}\right]\exp\left[-\frac{\sum_\alpha \hbar\omega^i_\alpha}{2k_B T}\right] \times$$

$$\sum_{n_\alpha,k_\alpha}\exp\left[-\frac{\sum_\alpha n\hbar\omega^i_\alpha}{k_B T}\right]\exp\left[-\frac{\theta(\sum_\alpha k\hbar\omega^f_\alpha - \sum_\alpha n\hbar\omega^i_\alpha)}{k_B T}\right] \times$$

$$|\langle\chi^f_{k_\alpha}|\chi^i_{n_\alpha}\rangle|^2 \quad (10)$$

where the quantity ΔE is the energy of the transition

$$\Delta E = \Delta I + \frac{1}{2}\sum_\alpha(\hbar\omega^f_\alpha - \hbar\omega^i_\alpha)$$

Introducing the quantity $\xi_\alpha(\theta)$ for a classical oscillator α

$$\xi_\alpha(\theta) = Z_{s\alpha}^{-1}\exp\left[-\frac{\hbar\omega^i_\alpha}{2k_B T}\right]\sum_{n_\alpha,k_\alpha}\exp\left[-\frac{n_\alpha\hbar\omega^i_\alpha}{k_B T}\right] \times$$

$$\exp\left[-\frac{\theta(k_\alpha\hbar\omega^f_\alpha - n_\alpha\hbar\omega^i_\alpha)}{k_B T}\right] \quad (11)$$

we rewrite eq 10 in a compact form

$$W = \frac{|V^i_{fi}|^2}{i\hbar k_B T Z_s Z_x Z_y}\int_{c-i\infty}^{c+i\infty} d\theta \exp\left[-\frac{\theta \Delta E}{k_B T}\right]\prod_\alpha \xi_\alpha(\theta) \times$$

$$\int dx\, dy \exp\left[\frac{(1-\theta)v_i(x) + \theta v_f(x)}{k_B T}\right]\exp$$

$$\left[\frac{(1-\theta)u_i(x) + \theta u_f(x)}{k_B T}\right] \quad (12)$$

The functions of the type of $\xi_\alpha(\theta)$ were calculated in general theory of nonadiabatic reactions developed in ref 43. According to the results of this reference, the function $\xi_\alpha(\theta)$ can be presented as follows

$$\xi_\alpha(\theta) = g_\alpha(\theta)\exp\left[-\frac{\phi_\alpha(\theta)E^f_{r\alpha}}{k_B T}\right] \quad (13)$$

where

$$\phi_\alpha(\theta) = \left(\frac{2k_B T}{\hbar\omega^f_\alpha}\right) \times$$

$$\frac{\tanh[\hbar\omega^f_\alpha\theta/(2k_B T)]\tanh[\hbar\omega^i_\alpha(1-\theta)/(2k_B T)]}{\tanh[\hbar\omega^f_\alpha\theta/(2k_B T)] + (\omega^f_\alpha/\omega^i_\alpha)\tanh[\hbar\omega^i_\alpha(1-\theta)/(2k_B T)]}$$

(14)

$$g_\alpha(\theta) = \frac{2}{\sqrt{\pi}}\left(\frac{\omega^f_\alpha}{\omega^i_\alpha}\right)^{1/2} \times$$

$$\frac{1 - \exp[-\hbar\omega^i_\alpha/(k_B T)]}{\{1-\exp[-2\hbar\omega^i_\alpha(1-\theta)/(k_B T)]\}^{1/2}\{1-\exp[-2\hbar\omega^f_\alpha\theta/(k_B T)]\}^{1/2}} \times$$

$$\left\{\coth\left[\frac{\hbar\omega^i_\alpha(1-\theta)}{2k_B T}\right] + \left(\frac{\omega^f_\alpha}{\omega^i_\alpha}\right)\coth\left[\frac{\hbar\omega^f_\alpha\theta}{2k_B T}\right]\right\}^{-1/2} \times$$

$$\left\{\frac{1}{\pi}\left(\tanh\left[\frac{\hbar\omega^i_\alpha(1-\theta)}{2k_B T}\right] + \left(\frac{\omega^f_\alpha}{\omega^i_\alpha}\right)\tanh\left[\frac{\hbar\omega^f_\alpha\theta}{2k_B T}\right]\right)\right\}^{-1/2} \quad (15)$$

$$E^f_{r\alpha} = \frac{\hbar\omega^f_\alpha}{2}(q^f_{\alpha 0f} - q^f_{\alpha 0i})^2 \quad (16)$$

where $q^f_{\alpha 0i}$ and $q^f_{\alpha 0f}$ are the initial and final equilibrium values of q_α coordinate in the final coordinate system. The quantity $E^f_{r\alpha}$ is called the local reorganization energy of an oscillator α. In general, it depends on x, however, and this effect is neglected in our theory.

Equation 12 is not suitable for practical applications yet, because it involves an infinite product of the functions ξ_α. To obtain an expression for the chemisorption rate constant in the closed form, we neglect the change in the course of reaction of the substrate oscillator frequencies that are *classical* according to our model, that is, it is assumed that $\omega^i_\alpha = \omega^f_\alpha \equiv \omega_\alpha$. In this assumption, the preexponential factor $g_\alpha(\theta)$ in eq 13 is equal to unity, and $\varphi_\alpha(\theta) = \theta(1-\theta)$. That allows us to replace approximately hyperbolic tangents by their arguments. Therefore, the product of ξ_α functions in eq 12 reduces to a simple form

$$\prod_\alpha \xi_\alpha(\theta) = \exp[-\theta(1-\theta)E_r/(k_B T)] \quad (17)$$

where E_r is the total reorganization energy for all classical modes of the substrate equal to the sum over α of the corresponding local reorganization energies

$$E_r = \sum E^f_{r\alpha} \quad (18)$$

The reorganization energy is an important kinetic parameter of the system characterizing a contribution of the vibration modes of the substrate to the activation energy of reaction.

Now we consider the integrals over x, y, and θ in eq 12 taking into account eq 17. The form of eq 5 implies the classical motion for x- and y-modes. However, the frequencies of intramolecular vibrations for diatomic molecules are usually rather high, and they exhibit quantum behavior already at room temperature. A more general formulation of the theory taking into account the quantum behavior of intramolecular vibrations exists.[34] The analysis shows that the main contribution to the transition probability for exothermic reactions comes then from the transitions from the initial ground vibrational state and the results are very close to those for the classical intramolecular modes presented below. The main difference consists of the fact that the reaction free energy involves the zero-point energy of the intramolecular modes. With these reservations, we shall treat x- and y- modes as classical ones.

The integrals can be calculated approximately using the saddle-point method.[34-36] This calculation leads to the following equation for the transition probability

$$W = \frac{(2\pi)^{3/2}(k_BT)^{1/2}|V_{fi}^i|^2}{\hbar Z_x Z_y \sqrt{f''_{1\hat{x}\hat{x}}f''_{2\hat{y}\hat{y}}|H''_{\hat{\theta}\hat{\theta}}|}} e^{-(\hat{\theta}[\Delta E + v_f(\hat{x}) + u_f(\hat{u})] + (1-\hat{\theta})[v_i(\hat{x}) + u_i(\hat{y})]/(k_BT))} \times$$

$$e^{-(\hat{\theta}(1-\hat{\theta})E_r/(k_BT))} \quad (19)$$

where $\hat{x}$, $\hat{y}$, and $\hat{\theta}$ are the coordinates of the saddle point determined by the equations

$$\Delta E = v_i(x) - v_f(x) + u_i(y) - u_f(y) + (2\theta - 1)E_r \quad (20)$$

$$(1 - \theta)\frac{dv_i(x)}{dx} + \theta\frac{dv_f(x)}{dx} = 0 \quad (21)$$

$$(1 - \theta)\frac{du_i(y)}{dy} + \theta\frac{du_f(y)}{dy} = 0 \quad (22)$$

$f''_{1\hat{x}\hat{x}}$ and $f''_{2\hat{y}\hat{y}}$ in eq 19 denote the partial second derivatives over x and y, respectively, of the functions

$$f_1(x,\theta) = \theta v_f(x) + (1 - \theta)v_i(x)$$

$$f_2(y,\theta) = \theta u_f(y) + (1 - \theta)u_i(y)$$

and $H''_{\hat{\theta}\hat{\theta}}$ is the total second derivative over θ of the function

$$H(x,y,\theta) = \theta\Delta E + \theta(1 - \theta)E_r + f_1(x,\theta) + f_2(y,\theta)$$

at the point $(\hat{x},\hat{y},\hat{\theta})$.

The matrix element $V_{fi}^i = \langle\varphi_f(\{r_k\};\hat{x},\hat{y},\hat{\theta}|V^i|\varphi_i(\{r_k\};\hat{x},\hat{y},\hat{\theta}\rangle$ of eq 19 determines the splitting of the nonadiabatic surfaces U_i and U_f at their crossing point. The approximate estimation of this splitting may be done in terms of the resonance interaction of X_2 molecule and metal. Specifically, if we use the semi-empirical London model[24] for a plane model system $X_1X_2M_3M_4$ and suppose that the sum of resonance integrals of the bonds X_1-X_2 and M_3-M_4 (denoted by a) is greater than that of the bonds X_1-M_4 and X_2-M_3 (denoted by b) and much greater than that of the cross bonds X_1-M_3 and X_2-M_4, we can find

$$V_{fi}^i \approx b(b/2a)$$

The expression for the activation energy $E_a = H(\hat{x},\hat{y},\hat{\theta})$ given by eq 19 can be rewritten in the equivalent form substituting eq 20 into the exponential factor of eq 19. We have

$$E_a = v_i(\hat{x}) + u_i(\hat{y}) + \hat{\theta}^2 E_r = v_i(\hat{x}) + u_i(\hat{y}) +$$
$$\frac{[\Delta E + v_f(\hat{x}) + u_f(\hat{y}) - v_i(\hat{x}) - u_i(\hat{y}) + E_r]^2}{4E_r} \quad (23)$$

The second term in eq 23 represents the contribution into E_a due to the extension of the bond X-X while the transition state is formed. There are contributions into E_a of the reaction energy ΔE and the reorganization energy of the substrate geometric structure E_r that are presented by the third term. Let us denote the effective reaction energy at the saddle point coordinate values $\hat{x}$ and $\hat{y}$ by $\Delta\tilde{E}$ according to eq 24

$$\Delta\tilde{E} = \Delta E + v_f(\hat{x}) + u_f(\hat{y}) - v_i(\hat{x}) - u_i(\hat{y}) \quad (24)$$

One can see from eq 23 that the derivative of the activation energy on the effective reaction energy is

$$\hat{\theta} = {}^1/_2 + \Delta\tilde{E}/(2E_r) \quad (25)$$

The factor $\hat{\theta}$ characterizes geometrically the symmetry of the system's potential energy surface in the neighborhood of the transition configuration. If the effective reaction energy $\Delta\tilde{E}$ is negligibly small, the symmetry factor $\hat{\theta}$ is about ${}^1/_2$ and the contribution into the activation energy of the squared term of eq 23 is mainly due to reorganization energy and approximately equal to $E_r/4$.

The above-considered nonadiabatic approach is appropriate if the electron matrix element $V_{fi}^i \equiv V$ is lower than k_BT (the more exact criteria may be found in ref 34). Nonadiabatic reactions are characterized by the low probability of the reorganization of the electron state at the transition configuration. On the contrary, if the matrix element $V \gg k_BT$, the change of positions of nuclei is adiabatically followed by electrons and the electron state reorganization probability is significant. In this case, the adiabatic reaction activation energy E_a^{ad} should be calculated with the use of an adiabatic surface U_- that has the following form (in two-level approximation)

$$U_- = ({}^1/_2)(U_i + U_f) - ({}^1/_2)\sqrt{(U_i - U_f)^2 + 4V^2}$$

The activation energy E_a^{ad} is determined as the difference between the saddle-point energy and the energy at the initial equilibrium configuration, that is,

$$E_a^{ad} = U_-(\hat{x},\hat{y},\hat{\theta}) - I_i$$

This equation may be approximately rewritten in the form (see ref 34)

$$E_a^{ad} \approx E_a - 2V\sqrt{\hat{\theta}(1 - \hat{\theta})}$$

where E_a is determined by eq 23 of the nonadiabatic theory and $\hat{\theta}$ is the symmetry factor of the diabatic terms.

In the present work, we consider only the nonadiabatic approach, assuming the matrix element V to be small, and the adiabatic theory will be the object of our next communication. This assumption is supported by the fact that the hydrogen dissociative reactions on palladium and possibly on other metals are characterized by the triplet-singlet transition.[41] This effect could reduce notably the splitting $2V$ of the diabatic surfaces U_i and U_f at the transition configuration.

4. Approximate Expressions for the Rate Constant

Both eqs 19 and 23 are rather general because the functions $v_{i,f}(x)$ and $u_{i,f}(y)$ were not specified yet. To calculate the rate constant of a specific system in an explicit form, one should take analytical expressions for these functions. However, with certain restrictions imposed on these functions, solution of eqs 21 and 22 for the system in question, that is, the formal calculation of the activation energy, can be performed without detailed information about the functions $v_{i,f}(x)$ and $u_{i,f}(y)$. This idea has been used in ref 44 in which the kinetics of nucleophilic substitution reactions in solution was considered, and it is used here for obtaining approximate expression of the dissociative adsorption rate constant as well.

So, let us discuss the functions $u_i(y)$ and $u_f(y)$ in more detail. We shall consider two particular cases.

Approximation a. In this approximation, we shall assume that the change of the potential energy $u_i(y)$ along the coordinate
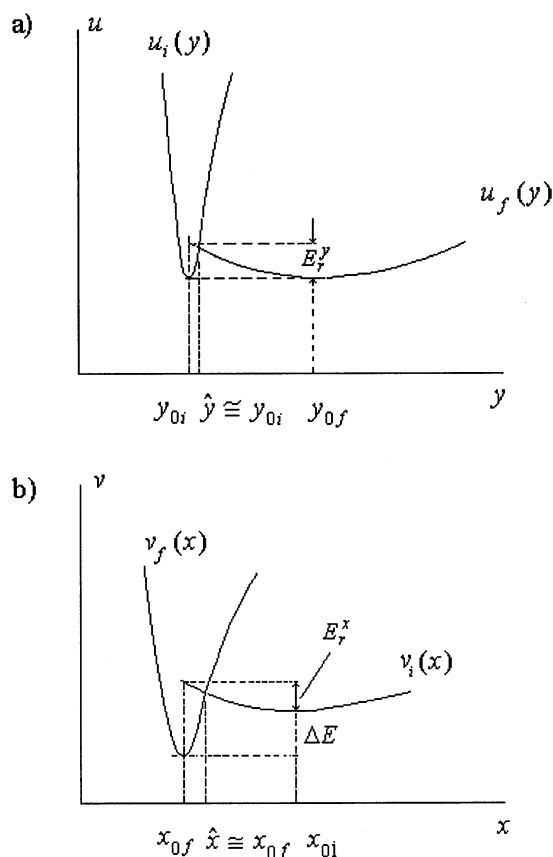
Theory of Dissociative Adsorption Kinetics

J. Phys. Chem. B, Vol. 106, No. 45, 2002 **11789**

a)

b)

Figure 2. Cross sections of the initial and final potential energy surfaces along x and y coordinates. E_r^x and E_r^y are the partial reorganization energies. The partial transition energy along x coordinate (cross section b) is equal to the total energy of the reaction, ΔE; the corresponding energy for y coordinate (cross section a) is equal to zero because the sum of the partial transition energies along all coordinates is equal to the total reaction energy.

y, beginning from the minimum point, is far more rapid than the corresponding change of the potential energy $u_f(y)$ along the same coordinate. In other words, the potential curve in the initial state is supposed to be steep and that in the final state to be smooth (Figure 2a). This assumption physically corresponds to the fact that the curve $u_i(y)$ is the potential well for the vibrations of tightly bonded atoms X−X and the curve $u_f(y)$ is the potential well for the vibrations of the same but weakly bonded atoms. For example, the X−X bond in a physisorbed molecule is slightly different from that in a free X_2 molecule, but in the chemisorbed molecule, the interaction between the X atoms is significantly weakened because of the cohesion of these atoms with a substrate.

The functions $v_i(x)$ and $v_f(x)$ describe the attractive intermolecular interaction of the reactant X_2 as a whole with the metal surface along the perpendicular direction. The reactant is at a larger distance from the metal in the initial equilibrium state than that in the final one. Therefore, the interaction will be weaker in the initial state than that in the final, that is, the potential well $v_f(x)$ will be deeper and steeper than the potential well $v_i(x)$ (Figure 2b). The form of the functions $v_i(x)$ and $v_f(x)$ shown in Figure 2b corresponds to the Lennard-Jones model[45] for the adsorption, which supposes that (1) the curve $v_i(x)$ has a shallow minimum at a large distance of the adsorbate molecule from the substrate and (2) cohesion between the individual atoms of the adsorbate molecule and the substrate is greater than the dissociation energy of the X_2 molecule.

As can be easily seen, for these forms of the potential curves $v_{i,f}(x)$ and $u_{i,f}(y)$, the approximate solutions of eqs 21 and 22 to determine the coordinates $\hat{x}$ and $\hat{y}$ of the saddle point are as follows (see Figure 2a,b)

$$\hat{y} \cong y_{0i} \qquad (26)$$

$$\hat{x} \cong x_{0f} \qquad (27)$$

Equation 26 means that the bond X−X in the adsorbate molecule is virtually nonstretched at the transition configuration, that is, the bond length $\hat{y}$ is almost equal its equilibrium value y_{0i} of the initial state. According to eq 27, the molecule X_2 itself in the transition configuration is near the substrate surface at the distance $\hat{x}$ that almost coincides with the value x_{0f} in the final equilibrium state. Qualitatively, this result may be understood from the fact that at $\theta \approx {}^1/_2$ the derivatives $(1 - \theta)\, dv_i/dx$ and $-\theta\, dv_f/dx$, as well as the derivatives $(1 - \theta)\, du_i/dy$ and $-\theta\, du_f/dy$, are equal to each other if the coordinates $\hat{x}$ and $\hat{y}$ almost coincide with those of the function minima, x_{0f} and y_{0i}, respectively.

In the neighborhood of the coordinates x_{0f} and y_{0i}, the potential curves $v_f(x)$ and $u_i(y)$ may be approximated by the parabolic functions, $v_f(x) = \mu(\Omega_f^x)^2(x - x_{0f})^2/2$ and $u_i(y) = M(\Omega_i^y)^2(y - y_{0i})^2/2$, and $v_i(x)$ and $u_f(y)$ by linear ones. The criteria for the latter approximations are

$$M(\Omega_i^y)^2 \gg u_f'' \qquad (28')$$

$$\mu(\Omega_f^x)^2 \gg v_i'' \qquad (28'')$$

where Ω_i^y and Ω_f^x are the vibration frequencies corresponding to the harmonic approximation of the functions $u_i(y)$ and $v_f(x)$, M and μ are the respective reduced masses, and u_f'' and v_i'' are the respective second derivatives of the functions. Furthermore, the criteria for validity of eqs 26 and 27 are that $u_i(\hat{y})$, $v_f(\hat{x}) < k_B T$. This means that the contributions to E_a from $u_i(\hat{y})$ and $v_f(\hat{x})$ may be neglected. When $u_i(y)$ and $v_f(x)$ are parabolic and $v_i(x)$ and $u_f(y)$ are linear, the exact solutions of eqs 21 and 22 have the form

$$\hat{x} = x_{0f} + \frac{\theta - 1}{\theta} \frac{v_i'(x_{0f})}{\mu(\Omega_f^x)^2} \qquad (29)$$

$$\hat{y} = y_{0i} + \frac{\theta}{1 - \theta} \frac{u_f'(y_{0i})}{M(\Omega_i^y)^2} \qquad (30)$$

Substitution of eqs 26 and 27 into eq 23 results in the following approximate expression for the activation energy

$$E_a \cong E_r^x + \frac{[\Delta E + E_r^y - E_r^x + E_r]^2}{4E_r} \qquad (31)$$

Here E_r^x and E_r^y denote the so-called reorganization energies along the coordinates x and y that are equal to $v_i(x_{0f}) - v_i(x_{0i})$ and $u_f(y_{0i}) - u_y(y_{0i})$, respectively (see Figure 2). If we take advantage of the harmonic approximation, the reorganization parameters E_r^x and E_r^y can be estimated by the following equations

$$E_r^x = \frac{1}{2}\mu(\Omega_i^x)^2(x_{0i} - x_{0f})^2$$

$$E_r^y = \frac{1}{2}M(\Omega_f^y)^2(y_{0f} - y_{0i})^2$$

The direct estimation of these reorganization energies can be obtained if the initial and final stationary states of the system are known. Then the energies E_r^x and E_r^y are equal to

$$E_r^x = E(x_{0f}, y_{0i}, \{q_{0i}\}) - E(x_{0i}, y_{0i}, \{q_{0i}\})$$

$$E_r^y = E(x_{0f}, y_{0i}, \{q_{0f}\}) - E(x_{0f}, y_{0f}, \{q_{0f}\})$$

where $E(x_{0f}, y_{0i}, \{q_{0i}\})$ is the energy of the system at the frozen initial equilibrium coordinates y_{0i} and $\{q_{0i}\}$ and the final equilibrium coordinate x_{0f} and $E(x_{0f}, y_{0i}, \{q_{0f}\})$ is that at the frozen final equilibrium coordinates y_{0f} and $\{q_{0f}\}$ and the initial equilibrium coordinate x_{0i}.

We note that while the bond X–X is practically nonstretched in the transition state, that is, there is no barrier along the coordinate y for the considered type of potentials u_i and u_f, the E_a dependence on the intramolecular properties of the adsorbate molecule appears through the reorganization parameter E_r^y. After the electron reorganization at the transition state, the molecule X_2 appears to be in an excited state. It is higher than the final equilibrium state by quantity E_r^y and the molecule must relax into the ground state releasing its energy to the bond X–X that is stretched in the final state.

One can approximately neglect the squared term over ΔE in eq 31 if the considered transition is characterized by small energy ΔE, so eq 31 reduces to the form

$$E_a = \hat{\theta} \Delta E + c \tag{31'}$$

where

$$c = E_r^x + (E_r + E_r^y - E_r^x)^2/(4E_r) \tag{31''}$$

and the factor $\hat{\theta}$ is given by eq 25 in which $\Delta\tilde{E} = \Delta E + E_r^y - E_r^x$. The first term in eq 31′ may be compared with the corresponding term of eq 1. However, the factor $\hat{\theta}$ in eq 31′ is generally not equal to $^1/_2$ and depends on transition energy.

The preexponential factor A of eq 19 is easily calculated in the considered approximation. Indeed, according ref 34, the configuration integrals over x and y coordinates can be written as

$$Z_x = \sqrt{\frac{2\pi k_B T}{(d^2 v_i/dx^2)_{x_{0i}}}} \quad \text{and} \quad Z_y = \sqrt{\frac{2\pi k_B T}{(d^2 u_i/dy^2)_{y_{0i}}}}$$

The second derivatives of the functions f_1, f_2, and H at the transition state are equal to

$$f_{1\hat{x}\hat{x}}'' \approx \hat{\theta} \mu (\Omega_f^x)^2$$

$$f_{2\hat{y}\hat{y}}'' = (1 - \hat{\theta}) M (\Omega_i^y)^2$$

$$|H_{\hat{\theta}\hat{\theta}}''| = 2E_r$$

Substituting these derivatives and the partitions functions Z_x and Z_y into the preexponential factor of eq 19, we find that

$$A = \frac{|V_{fi}^i|^2 (\Omega_i^x/\Omega_f^y)}{\hbar\sqrt{\hat{\theta}(1 - \hat{\theta})E_r k_B T/\pi}} \equiv \frac{k_B T}{\hbar} \kappa \exp\left(\frac{\Delta\hat{S}}{k_B}\right) \tag{32}$$

where $\Delta\hat{S}/k_B$ denotes the activation entropy due to the change

of the vibration frequency Ω_f^x in the final state in comparison with the initial state

$$\Delta\hat{S}/k_B = \log_e(\Omega_i^x/\Omega_f^y) \tag{33}$$

and κ is the transmission coefficient that for the nonadiabatic reactions is equal to

$$\kappa = \frac{|V_{fi}^i|^2}{k_B T\sqrt{\hat{\theta}(1 - \hat{\theta})E_r k_B T/(4\pi^3)}} \equiv \frac{|V_{fi}^i|^2}{V_{cr}^2} \tag{34}$$

For the adiabatic reactions, $\kappa = 1$, the adiabaticity criterion is determined as[34]

$$|V_{fi}^i|^2/V_{cr}^2 \geq 1 \tag{35}$$

Approximation b. Now we shall consider the equation for the activation energy if the criterion 28″ is not fulfilled but the criterion 28′ is still valid. In this case, we should solve eqs 20 and 21 for specific potentials $v_i(x)$ and $v_f(x)$ that may be approximated, for example, by Morse functions. So, let the functions $v_i(x)$ and $v_f(x)$ have the form

$$v_i(x) = D_i[1 - e^{-\beta_i(x-x_{0i})}]^2 \tag{36'}$$

$$v_f(x) = D_f[1 - e^{-\beta_f(x-x_{0f})}]^2 \tag{36''}$$

where D_i, D_f and β_i, β_f are the dissociation energies and the anharmonicity parameters that must be taken from experimental data or quantum chemical calculations. β_i and β_f in eqs 36 are expressed through the effective mass μ of the vibration, frequencies Ω_i^x, Ω_f^x, and energies D_i, D_f

$$\beta_{i,f} = [\mu(\Omega_{i,f}^x)^2/(2D_{i,f})]^{1/2} \tag{37}$$

Here the frequencies Ω_i^x and Ω_f^x characterize vibrations of X_2 molecule as a whole with respect to the substrate surface in the physisorbed (initial) and chemisorbed (final) states. Introducing notations

$$t = \beta_i/\beta_f \tag{38}$$

$$\gamma = \exp[\beta_i(x_{0i} - x_{0f})] \tag{39}$$

$$z = \exp[-\beta_f(x - x_{0f})] \tag{40}$$

we rewrite the functions $v_i(x)$ and $v_f(x)$ as follows

$$v_i[z(x)] = D_i(1 - \gamma z^t)^2 \tag{41'}$$

$$v_f[z(x)] = D_f(1 - z)^2 \tag{41''}$$

In these equations, the value of z changes between unity and zero if x changes in the interval $x_{0f} \leq x < \infty$.

Now, substitution of eqs 41′ and 41″ into eqs 20 and 21 leads to the set of two equations that determine two coordinates, $\hat{z}(\hat{x})$ and $\hat{\theta}$, at the saddle point in terms of the structure and energetic characteristics of the system

$$\hat{\theta} = \frac{tD_i(\gamma^2\hat{z}^{2t-1} - \gamma\hat{z}^{t-1})}{D_f(1 - \hat{z}) + tD_i(\gamma^2\hat{z}^{2t-1} - \gamma\hat{z}^{t-1})} \tag{42}$$

$$\Delta E = D_i(1 - \gamma\hat{z}^t)^2 - D_f(1 - \hat{z})^2 - E_r^y + (2\hat{\theta} - 1)E_r \tag{43}$$

Theory of Dissociative Adsorption Kinetics

J. Phys. Chem. B, Vol. 106, No. 45, 2002 **11791**

Equations 42 and 43 can be solved by a simple computation procedure. The values of $\hat{z}(\hat{x})$ and $\hat{\theta}$ calculated from these equations along with the value of $\hat{y}$ from eq 26 being substituted in the general eq 23 give the activation energy in the form

$$
E_a = D_i(1 - \gamma\hat{z}^t)^2 + \\
\frac{[\Delta E + E_r^y + D_f(1 - \hat{z})^2 - D_i(1 - \gamma\hat{z}^t)^2 + E_r]^2}{4E_r} \quad (44')
$$

where $E_r^y = u_f(y_{0i})$. Simple manipulations allow analyzing the dependency of the activation energy on the reaction energy ΔE. At arbitrary $\hat{z}$ (in the interval $0 < \hat{z} < 1$), $\hat{\theta}$ is calculated according to eq 42. Then, substitution of the latter into eqs 43 and 44′ gives the corresponding values of E_a and ΔE.

The preexponential factor in the approximation b differs from that in the approximation a by the equations for Z_x, $f''_{1,\hat{x}\hat{x}}$, and $H''_{\theta\theta}$, which in this case are equal to

$$
Z_x = (\pi k_B T / \beta_i^2 D_i)^{1/2} \quad (45)
$$

$$
\frac{\partial^2 f_1}{\partial x^2}\bigg|_{\hat{x}} = 2\beta_i^2 D_i(1 - \hat{\theta})(2\gamma^2\hat{z}^{2t} - \gamma\hat{z}^t) + 2\beta_f^2 D_f\hat{\theta}(2\hat{z}^2 - \hat{z}) \quad (46)
$$

$$
\frac{d^2 H}{d\theta^2}\bigg|_{\hat{\theta}(\hat{x},\hat{y})} = -2E_r - \left(\frac{\partial v_i}{\partial x} - \frac{\partial v_f}{\partial x}\right)\bigg|_{\hat{x}}\frac{d\hat{x}}{d\theta} \quad (47)
$$

where the dependence of x on θ is determined by eqs 42 and 43. Substitution of eqs 45−47 into eq 19 along with previous formulas for Z_y and $f''_{2,\hat{x}\hat{x}}$ leads to the following expressions for the entropy term and V_{cr}^2 of the preexponential factor (cf. with eqs 33 and 34)

$$
\Delta\hat{S}/k_B = \log_e \frac{\sqrt{2\beta_i^2 D_i}}{(\partial^2 f_1/\partial x^2)^{1/2}|_{\hat{x}}} \quad (48)
$$

$$
V_{cr}^2 = k_B T \sqrt{(1 - \hat{\theta})k_B T |H''_{\theta\theta}| / (8\pi^3)} \quad (49)
$$

In the special case when the initial state is the molecular adsorption and the dissociative state is the final one, eq 44′ may be rewritten with the use of so-called binding energy, E_{bind}, shown in Figure 3. We can see that this quantity is determined as the difference

$$
E_{bind} = E_i(X_2 + S) - E_f(X\cdots X\cdots S)
$$

where $(X_2 + S)$ are the reactants at an infinitely long distance and $(X\cdots X\cdots S)$ is the dissociated molecule on the surface S. The relations 50 and 51 follow from Figure 3

$$
\Delta E = -E_{bind} + D_i \quad (50)
$$

$$
D_f = D_{X_2} + E_{bind} \quad (51)
$$

where D_{X_2} is the dissociate energy of X_2 in gas phase and the quantity D_i is indeed the heat (Q_{X_2}) for the adsorption of the
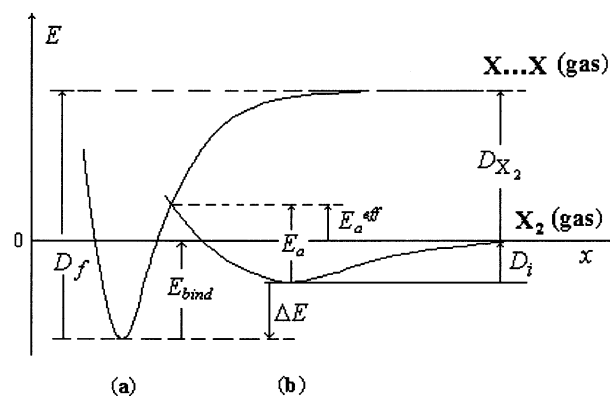

Figure 3. Minimum energy path along x coordinate. Points a and b denote the dissociated and physisorbed states, respectively; E_a^{eff} is the effective activation energy relative to reactants; E_a is the activation energy for the dissociative state relative to the physisorbed state.

X_2 molecule on the surface S. Inserting eqs 50 and 51 into eq 44′, we obtain

$$
E_a = Q_{X_2}(1 - \gamma\hat{z}^t)^2 + \\
\frac{[Q_{X_2}[2\gamma\hat{z}^t - (\gamma\hat{z}^t)^2] + E_r^y + D_{X_2}(1 - \hat{z})^2 - E_{bind}(2\hat{z} - z^2) + E_r]^2}{4E_r} \quad (44'')
$$

The heat Q_{X_2} of the molecular adsorption is usually small (approximately several kilocalories per mole). So, for the adsorption processes with the high activation energy, the second item in eq 44″ plays the more important role than the first one. Now, let the interaction energy of a chemisorbed molecule with the surface be higher for a metal M_1 than for a metal M_2, that is, the binding energy for the metal M_2 is greater than that for the metal M_1. Evidently, one should expect a larger reorganization of the adsorption site for the first metal than for the second one and, therefore, an increase of the reorganization parameter E_r in this sequence. According to eq 44″, the increase of the binding energy reduces the corresponding activation barrier and the increase of E_r leads to the increase of E_a, that is, these parameters affect the activation energy in an opposite way. Therefore, if we neglect the small change of the first term in numerator of eq 44″, the resulting effect of the specific metal property on the E_a will be determined by competition of the E_r and E_{bind}.

5. Example

As it was mentioned in Introduction, in the general case, the dissociative adsorption process may proceed via a number of adsorption intermediates. Thus, the reaction mechanism can be described by the following scheme:
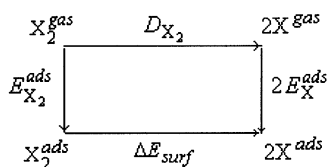
$$
X_2^{gas} \rightleftharpoons X_2^{ads,1} \rightleftharpoons X_2^{ads,2} \rightleftharpoons \ldots 2X^{ads}
$$
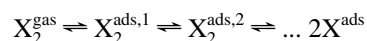
where $2X^{ads}$ is the dissociated state and $X_2^{ads,1}$, $X_2^{ads,2}$, etc. are the states characterized by different cohesion energies of X_2 with a surface; the number of the intermediates depends on the nature of reactants and on the surface structure. The accurate analysis of this adsorption reaction kinetics requires the calculations of transition probabilities for all intermediate steps or, at least, for the limiting step of the process. However, such analysis is beyond the scope of the present work, and we restrict ourselves to the simplest mechanism assuming that weakly interacting with a surface molecular state converts directly to

the dissociated (atomic) state. This scheme is as a rule employed in other works, particularly, in the BOC-MP/UBI-QEP model[25,26] and is widely applied for semiquantitative estimations of the activation barriers.[27−33] The minimum energy path for this reaction mechanism is shown in Figure 3.

In the simple model of adsorption, the reaction energy ΔE of eqs 31 or 44 is that of the surface reaction

$$X_2{}^{ads} \leftrightarrow 2X^{ads}$$
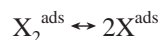
Thus, the energy $\Delta E \equiv \Delta E_{surf}$ is connected with other adsorption characteristics by the following thermodynamic cycle

$$
\begin{array}{ccc}
X_2{}^{gas} & \xrightarrow{D_{X_2}} & 2X^{gas} \\
\big\downarrow{\scriptstyle E_{X_2}^{ads}} & & \big\downarrow{\scriptstyle 2E_X^{ads}} \\
X_2{}^{ads} & \xrightarrow{\Delta E_{surf}} & 2X^{ads}
\end{array}
$$

Here E_X^{ads} and $E_{X_2}^{ads}$ are the adsorption energies of X atom and X_2 molecule, respectively; D_{X_2} is the dissociation energy of X_2 molecule in gas phase. It follows from this cycle that

$$\Delta E = D_{X_2} + 2E_X^{ads} - E_{X_2}^{ads} \equiv D_{X_2} - 2Q_X + Q_{X_2} = $$
$$Q_{X_2} - E_{bind} \quad (52)$$

where $-E_{bind} = D_{X_2} + 2E_X^{ads}$ is the binding energy, and Q_k denotes the corresponding heat effect.

Now, let X_2 be a hydrogen molecule that interacts with a palladium surface. For this system, two quantities of eq 52 are well-known from experiments. They are $D_{H_2} = 104$ kcal/mol[46] and the binding energy, ranging from 20.8 to 24.4 kcal/mol for low-index single-crystal palladium surface.[47,48] In our estimations, we use $E_{bind} = 20.8$ kcal/mol, which is the initial adsorption energy on Pd(111) surface. As for value of Q_{H_2}, we should note the following.

Existence of the molecular preadsorption state preceding the hydrogen dissociation on palladium is extensively discussed in the literature. The six-dimensional quantum dynamical calculations[49−51] show that the experimentally observed initial decrease of the sticking probability with increasing kinetic energy,[52] which is usually attributed to the precursor mechanism, could be explained by dynamical steering. That led the authors[49] to the conclusion that there is "no need for a molecular precursor adsorption state." This point of view is widely accepted in the modern literature (see, for example, reviews 7, 15, and 53). On the other hand, a well-defined weakly bound state of adsorbed hydrogen characterized by the first-order desorption kinetics and positive adsorbent-induced change in the surface work function was observed on palladium black,[54,55] on thin palladium film,[56,57] on various Pd samples including supported ones,[58] and on stepped surfaces.[59] Similarly, the local minima corresponding to the molecular adsorption states were localized in the DFT studies of hydrogen dissociation on all low-index Pd surfaces.[60−62] Moreover, the experimental and the theoretical data of hydrogen dissociation on the Pd(111) surface with subsurface V led the authors[63] to the recognition that "there is a true precursor for hydrogen adsorption after all". Depending on the surface structure, the potential well for this state varies in the range from 4.5 to 8.7 kcal/mol with more stable complexes found on more "open" faces. In our estimates, we used $Q_{H_2} = 4.9$ kcal/mol. This value after substitution into eq 50 leads to the energy $\Delta E = -15.9$ kcal/mol. This presents an approximate estimation of the heat effect of the reaction.

Now let us consider quantitative characteristics of the potential curves $u_i(y)$, $u_f(y)$ and $v_i(x)$, $v_f(x)$, which appear in equations for the activation energy, eqs 31 or 41, or eq 44 directly and via the local reorganization energies E_r^x and E_r^y. The characteristic frequency Ω_i^y of the intramolecular potential $u_i(y)$ for the weakly bonded molecular adsorption state is apparently close to the H−H vibration frequency in the free H_2 molecule equal to 4160 cm^{-1},[46] and the corresponding value of y_{0i} is close to the equilibrium bond length in the hydrogen molecule and is taken to be equal to 0.78 Å because the H−H bond is only slightly disturbed in this adsorbed state as compared to the free molecule. The final equilibrium distance H···H in the dissociated state, y_{0f}, is determined by the substrate surface structure and by an arrangement of the adsorption sites. In the particular case of palladium surfaces, the minimal value of y_{0f}, which is equal to 2.75 Å, corresponds to the nearest fcc sites on Pd(111) surface. On more "open" surfaces and at lower coverage, the most stable adsorption positions are even more distant. At such large distances, the attractive interaction between dissociated H-atoms is very small and the corresponding potential curve has the shallow minimum. So, for our estimations, we take the characteristic frequency Ω_f^y equal to $\sim k_B T/\hbar$.

The point of minimum, x_{0i}, of the intermolecular potential curve $v_i(x)$ (Figure 2b) is determined by the equilibrium distance between the molecularly adsorbed H_2 and metal surface. This distance was calculated to be 1.85 Å for Pd(111) surface.[60] As a corresponding characteristic frequency Ω_i^x of the potential $v_i(x)$ for the weakly adsorbed state, it seems to be reasonable to take thermal frequency $\sim k_B T/\hbar$. The characteristic frequency Ω_f^x of the potential $v_f(x)$ for the chemisorbed state closely corresponds to the frequency of the perpendicular vibrations of the adsorbed H atoms on palladium surface, $\omega_\perp$. This frequency was found to be equal to ~ 1000 cm^{-1} in high-resolution electron energy-loss spectroscopy (HREELS) experiments[64,65] for the Pd-(110) surface. Quantum chemical calculation[66] of the full three-dimensional potential energy surface of H on Pd(111) for the fcc site leads to $\omega_\perp = 1054$ cm^{-1}. This frequency was used in our numerical calculations because the corresponding structure is closer to our geometry. The height of atomic hydrogen adsorption above the metal surface (h) characterizes the equilibrium distance x_{0f} in the final dissociated state. The h value apparently strongly depends on the surface structure and the adsorption position on it. According to the experimental data[67−69] and theoretical calculation,[70] h falls within the range from 0.2 to 0.87 Å. In our estimations, we set h value to be 0.75 Å as it was determined by the low-energy electron diffraction (LEED) experiment for hydrogen adsorption on Pd(111).[67]

As was pointed out above, the parameter D_i is the adsorption heat in our model, and for hydrogen molecule on palladium is equal to 4.9 kcal/mol. The parameter D_f may be calculated by eq 51. The substitution of the corresponding values of the dissociation and binding energies into this equation gives $D_f = 124.8$ kcal/mol.

The last parameter that we have to consider is the substrate reorganization energy, E_r, given by eqs 16 and 18. We need to know the structure and frequency data about the adsorption site with the weakly bonded and chemisorbed hydrogen molecule to calculate numerically the energy E_r. This information may be drawn from the corresponding quantum chemical calculations on a model that in the greater possible extent would take into account the structure changes that accompany the transition between two adsorption states. In our approximate estimations of this quantity, we restrict ourselves by consideration of several

Theory of Dissociative Adsorption Kinetics

J. Phys. Chem. B, Vol. 106, No. 45, 2002 **11793**

TABLE 1: Values of the Parameters Used To Calculate the Activation Energy[a]

item	value	refs
E_{bind}	20.8	46, 47
E_{r}	11	
D_{H_2}	104	45
Q_{H_2}	4.9	63
$\Omega_{\text{i}}^{x}, \Omega_{\text{f}}^{y}$	208	
Ω_{f}^{x}	1054	64, 65
Ω_{i}^{y}	4160	45
$x_{0\text{i}}$	1.85	60
$x_{0\text{f}}$	0.75	66−69
$y_{0\text{i}}$	0.78	45
$y_{0\text{f}}$	2.75	3

[a] Energies E_{r}, E_{bind}, D_{H_2}, and Q_{H_2} in kcal/mol, frequencies $\Omega_{\text{i,f}}^{x}$ and $\Omega_{\text{i,f}}^{y}$ in cm^{-1}, distances $x_{0\text{i}}$, $x_{0\text{f}}$ and $y_{0\text{i}}$, $y_{0\text{f}}$ in Å.

planar complexes containing five, seven, and nine palladium atoms and the tetrahedral cluster of the structure studied in the previous paper.[41] In these calculations, we used the DFT/B3LYP method as it is implemented in Gaussian 94[71] with basis LANL2 DZ for palladium and cc-pVDZ for hydrogen. Estimated values of the reorganization energy were in the range between 3 and 12 kcal/mol. The value of 11 kcal/mol seems to be reasonable to calculate the activation energy.

Now we are in the position to calculate the activation energy of the considered reaction using the values of parameters that were discussed above. These parameters (see Table 1) being substituted into eqs 31 and 44 give the values of E_{a} equal to 4.5 and 5.1 kcal/mol, respectively. The effective activation energy that may be directly compared with experimental data (see Figure 3) is

$$E_{\text{a}}^{\text{eff}} = E_{\text{a}} - D_{\text{i}}$$

Thus, we obtain $E_{\text{a}}^{\text{eff}} = 0.3$ kcal/mol in the approximation a and -0.6 kcal/mol in the Morse approximation b. According to our calculations, the symmetry factor $\theta = \partial E_{\text{a}}/\partial \Delta E$ is negative in the approximation a and is equal to 0.24 in the approximation b. The negative value of the symmetry factor obtained in the more rough model a means that we have to use the more accurate approximation b for the relevant describing of the considered system. This approximation gives the $E_{\text{a}}^{\text{eff}}$ value that seems to be in the reasonable agreement with the experimental data,[17,18] supporting that the considered reaction has no activation barrier. It is worth noting that the nonadiabatic theory would lead to some overestimation of the activation energy by a half value of the splitting energy of the diabatic terms at the crossing point. This reduction of the activation barrier is neglected in our approach.

According to our calculations in the model b, the position $\hat{x}$ of the molecule H$_2$ above the surface is equal to 1.16 Å at the transition state (so-called early barrier). This value of $\hat{x}$ is in reasonable agreement with result of ref 60 in which the potential surface of H$_2$ at Pd(111) was constructed by the DFT method. Specifically, for the fcc-fcc H$_2$ molecule orientation, which is the most appropriate for our model, the values of the transition configuration coordinates $\hat{x}$ and $\hat{y}$ and the activation energy were found[60] to be equal to 1.38 and 1.06 Å and -2 kcal/mol, respectively (compare with our values 1.16 and 0.78 Å and -0.6 kcal/mol). The value of $\hat{y} = 1.06$ Å is slightly greater than our approximate value (0.78 Å) (see eq 26). Thus, the elongation of H−H bond is not favorable under formation of the transition state because of high value of its force constant.

The earlier transition states of the H$_2$/palladium system along the x coordinate were found in other quantum chemical calculations of the potential energy surfaces: $\hat{x} = 1.42$ Å[61] for the surface Pd(100), and $\hat{x} = 1.36$ Å[62] for the surface Pd(110). However, the geometry of these model surfaces to a less extent corresponds to the parameters of our model used for numerical estimations. Therefore, direct comparison of our results with those of refs 61 and 62 is not accurate.

One important fact should be pointed out yet. In the works cited above, the calculations of the electron structures have been performed under fixed bond lengths Pd−Pd, in contrast to our model in which the structure reorganization of the adsorption sites was taken into account. This effect may play a role under comparison of our results and electron structure calculations.

The calculated value in the approximation b of the symmetry factor $\hat{\theta}$ differs considerably from the constant value $^1/_2$ in the phenomenological approach[25,26] (see eq 1).

Conclusions

A simple and useful method was suggested for calculation of the rate constant of the dissociative adsorption of a X$_2$ molecule on a metal surface taking into account a structure reorganization of the substrate. The consideration was performed in terms of the semiclassical nonadiabatic theory of chemical reactions for reactant interaction potentials of a general form, as well as with the use of the Morse approximation for the intermolecular potentials $v_{\text{i}}(x)$ and $v_{\text{f}}(x)$ characterizing the interaction of the X$_2$ and metal. Equations for the activation energy and preexponential factor are presented. Simplified expressions for these quantities are obtained under certain restrictions imposed on the potentials. It is shown that the kinetic characteristics calculated by these equations agreed well with those obtained for the Morse potentials. Numerical estimations made for the dissociative adsorption of a hydrogen molecule on a palladium metal show that the effect of the metal structure reorganization plays the important role for these processes.

References and Notes

(1) Somorjai, G. *Introduction to Surface Chemistry and Catalysis*; Wiley: New York, 1994.
(2) Coq, B.; Figueras, F. *J. Mol. Catal. A* **2001**, *173*, 117.
(3) Efremenko, I. *J. Mol. Catal. A* **2001**, *173*, 19.
(4) Brown, W. A.; Kose, R.; King, D. A. *Chem. Rev.* **1998**, *98*, 797.
(5) van Santen, R. A.; Neurock, M. *Catal. Rev. Sci. Technol.* **1995**, *37*, 557.
(6) Whitten, J. L.; Yang, H. *Surf. Sci. Rep.* **1996**, *24*, 55.
(7) Scheffler, M.; Stampfl, C. In *Handbook of Surface Science*; Horn, K., Scheffler, M., Eds.; Elsevier: Amsterdam, 1999; Vol. 2.
(8) Imbihl, R.; Demuth, J. E. *Surf. Sci.* **1986**, *173*, 354.
(9) Schmidt, J.; Stuhlman, Ch.; Ibach, H. *Surf. Sci.* **1993**, *284*, 121.
(10) Luntz, A. C.; Grimblot, J.; Fouler, D. E. *Phys. Rev. B* **1989**, *39*, 12903.
(11) Andersson, S.; Harris, J. E. *Phys. Rev. Lett.* **1982**, *48*, 545.
(12) Avouris, P.; Schmeisser, D.; Demuth, J. E. *Phys. Rev. Lett.* **1982**, *48*, 199.
(13) Kolasinski, K. W.; Cemic, F.; Hasselbrink, E. *Chem. Phys. Lett.* **1994**, *219*, 113.
(14) Steininger, H.; Lehwald, S.; Ibach, H. *Surf. Sci.* **1982**, *123*, 1.

(15) Diño, W. A.; Kasai, H.; Okiji, A. *Prog. Surf. Sci.* **2000**, *63*, 63.

(16) Gross, A. *Surf. Sci. Rep.* **1998**, *32*, 291.

(17) Luntz, A. C.; Brown, J. K.; Williams, M. D. *J. Chem. Phys.* **1990**, *93*, 5240.

(18) Christman, K.; Ertl, G.; Pignet, T. *Surf. Sci.* **1976**, *54*, 365.

(19) Nolan, P. D.; Lutz, B. P.; Tanaka, P. L.; Mullins, C. B. *Surf. Sci.* **1998**, *419*, L107.

(20) Winkler, A.; Guo, X.; Siddiqui, H. R.; Hagans, P. L.; Yates, Y. T. *Surf. Sci.* **1988**, *201*, 419.

(21) Campbell, C. T.; Ertl, G.; Kuipers, H.; Segmor, J. *Surf. Sci.* **1981**, *107*, 220.

(22) Whitten, J. L.; Yang, H. *Surf. Sci. Rep.* **1996**, *24*, 55.

(23) Liu, Z.-P.; Hu, P. *J. Chem. Phys.* **2001**, *115*, 4977.

(24) Glasstone, S.; Laidler, K. J.; Eyring, H. *The Theory of Rate Processes*; McGraw-Hill Book Co. Inc.: New York, 1941.

(25) Shustorovich, E. *Adv. Catal.* **1990**, *37*, 101.

(26) Shustorovich, E.; Sellers, H. *Surf. Sci. Rep.* **1998**, *31*, 1.

(27) Bensiger, J. B. In *Metal-Surface Reaction Energetics*; Shustorovich, E., Ed.; VCH Publishers Inc.: New York, 1991; p 53.

(28) Baetzold, R. In *Metal-Surface Reaction Energetics*; Shustorovich, E., Ed.; VCH Publishers Inc.: New York, 1991; p 109.

(29) Bell, A. In *Metal-Surface Reaction Energetics*; Shustorovich, E., Ed.; VCH Publishers Inc.: New York, 1991; p 191.

(30) (a) Zeigarnik, A. V.; Valdés-Pérez, R. E.; Myatkovskaya, O. N. *J. Phys. Chem. B* **2000**, *104*, 10578. (b) Zeigarnik, A. V.; Valdés-Pérez, R. E.; Egorova, N. I. *Surf. Sci.* **2001**, *487*, 146.

(31) (a) Azizian, S.; Gobal, F. *Langmuir* **2001**, *17*, 583. (b) Azizian, S.; Gobal, F. *Langmuir* **2000**, *16*, 8095. (c) Hei, M. J.; Chen, H. B.; Yi, J.; Lin, Y. J.; Lin, Y. Z.; Wei, G.; Liao, D. W. *Surf. Sci.* **1998**, *417*, 82. (d) Hei, M. J.; Chen, H. B.; Yi, J.; Lin, Y. J.; Lin, Y. Z.; Wei, G.; Liao, D. W. *Surf. Sci.* **1998**, *417*, 82.

(32) (a) Ishikawa, Y.; Liao, M.-S.; Cabrera, C. R. *Surf. Sci.* **2000**, *463*, 66. (b) Au, C.-T.; Zhou, T.-J.; Lai, W.-J. *Catal. Lett.* **1999**, *62*, 147. (c) Au, C.-T.; Ng, C.-F.; Liao, M.-S. *J. Catal.* **1999**, 185. (d) Liao M.-S.; Zhang, O.-F. *J. Mol. Catal. A.* **1998**, *136*, 185. (e) Liao, M.-S.; Au, C.-T.; Ng, C.-F. *Chem. Phys. Lett.* **1997**, *272*, 445.

(33) (a) Hansen, E.; Neurock, M. *Chem. Eng. Sci.* **1999**, *54*, 3411. (b) Hansen, E.; Neurock, M. *Surf. Sci.* **2000**, *464*, 91. (c) Hansen, E.; Neurock, M. *J. Phys. Chem. B* **2001**, *105*, 9218.

(34) Kuznetsov, A. M. *Charge Transfer in Physics, Chemistry and Biology*; Gordon & Breach: Reading, U.K., 1995.

(35) Kuznetsov, A. M.; Ulstrup, J. *Electron Transfer in Chemistry and Biology*, John Wiley & Sons: New York, 1999.

(36) Kuznetsov, A. M. *Stochastic and Dynamic Views of Chemical Reaction Kinetics in Solutions*; Press polytechniques et universitaires romandes: Lausanne, Switzerland, 1999.

(37) Fain, B. *Theory of Rate Processes in Condensed Media*; Springer: Berlin, 1980.

(38) Lee, W. T.; Ford, L.; Blowers, P.; Nigg, H. L.; Masel, R. I. *Surf. Sci.* **1998**, *416*, 141.

(39) Efremenko I.; Sheintuch, M. Unpublished results.

(40) Wilke, S.; Scheffler, M. *Phys. Rev. B* **1996**, *53*, 4926.

(41) German, E. D.; Efremenko, I.; Sheintuch, M. *J. Phys. Chem. A* **2001**, *105*, 11312.

(42) Landau, L. D.; Lifshitz, E. M. *Quantum Mechanics*; Pergamon: Oxford, U.K., 1965.

(43) Dogonadze, R. R.; Kuznetsov, A. M.; Vorotyntsev, M. A. *Phys. Status Solidi B* **1972**, *54*, 125, 425.

(44) German, E. D.; Dogonadze, R. R. *Int. J. Chem. Kinet.* **1974**, *6*, 457.

(45) Lennard-Jones, J. E. *Trans. Faraday Soc.* **1932**, *28*, 333.

(46) *Handbook of Chemistry and Physics*, 55th ed.; Lide, D. R., Ed; CRC Press: Boca Raton, FL, 1974−1975.

(47) Conrad, H.; Ertl, G.; Latta, E. E. *Surf. Sci.* **1974**, *41*, 435.

(48) Behm, R. J.; Christmann, K.; Ertl, G. *Surf. Sci.* **1980**, *99*, 320.

(49) Gross, A.; Wilke, S.; Scheffler, M. *Surf. Sci.* **1996**, *357*, 614.

(50) Gross, A.; Wilke, S.; Scheffler, M. *Phys. Rev. Lett.* **1995**, *75*, 2718.

(51) Gross, A. *Surf. Sci.* **1996**, *363*, 1.

(52) Rendulic, K. D.; Anger, G.; Winkler, A. *Surf. Sci.* **1989**, *208*, 404.

(53) Gross, A. *Surf. Sci. Rev.* **1998**, *32*, 291.

(54) Popova, N. M.; Babenkova, L. V. *React. Kinet. Catal. Lett.* **1979**, *11*, 187.

(55) Kiperman, S. L.; Gaidai, N. A. *Bulg. Chem. Commun.* **1998**, *30*, 242.

(56) Dus, R.; Nowicka, E. *Langmuir* **2000**, *16*, 584.

(57) Nowicka, E.; Dus, R. *Prog. Surf. Sci.* **1995**, *48*, 3.

(58) Konvalinka, J. A.; Scholten, J. J. F. *J. Catal.* **1977**, *48*, 374.

(59) Schmidt, P. K.; Christmann, K.; Kresse, G.; Hafner, J.; Lischka, M.; Gross, A. *Phys. Rev. Lett.* **2001**, *87*, 096103.

(60) Dong, W.; Hafner, J. *Phys. Rev. B* **1997**, *56*, 15396.

(61) Eichler, A.; Kresse, G.; Hafner, J. *Surf. Sci.* **1998**, *397*, 116.

(62) Ledentu, V.; Dong, W.; Sautet P. *Surf. Sci.* **1998**, *412*, 518.

(63) Beutl, M.; Lesnik, J.; Rendulic, K. D.; Hirschl, R.; Eichler, A.; Kresse, G.; Hafner, J. *Chem. Phys. Lett.* **2001**, *342*, 473.

(64) Conrad, H.; Kordesch, M. E.; Scala, R.; Stenzel, W. *J. Electron Spectrosc. Relat. Phenom.* **1986**, *38*, 289. Cited in: Richter, L. J.; Ho, W. *Phys. Rev. B* **1987**, *36*, 9797.

(65) Ellis, T. H.; Morin, M. *Surf. Sci.* **1989**, *216*, L351.

(66) Lovik, O. M.; Otsen, R. A. *Phys. Rev. B* **1998**, *58*, 10890.

(67) Felter, T. E.; Sowa, E. C.; van Hove, M. A. *Phys. Rev. B* **1989**, *40*, 891.

(68) Besenbacher, F.; Stensgaard, I.; Mortsen, K. *Surf. Sci.* **1987**, *191*, 288.

(69) Unezawa, K.; Ito, T.; Asada, M.; Nakanishi, S.; Ding, P.; Langford, W. A.; Hjorvarsson, B. *Surf. Sci.* **1997**, *387*, 320.

(70) Dong, W.; Ledentu, V.; Sautet, P.; Eichler, A.; Hafner, J. *Surf. Sci.* **1998**, *411*, 123.

(71) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, revision A.1; Gaussian, Inc.: Pittsburgh, PA, 1995.