NONADIABATIC RATE PROCESSES ON METAL SURFACE: LIMITATION BY SPIN CONVERSION

V. P. Zhdanov [*a,b]

[a] *Department of Applied Physics, Chalmers University of Technology*
S-41296, Göteborg, Sweden

[b] *Boreskov Institute of Catalysis, Russian Academy of Sciences*
630090, Novosibirsk, Russia

Rate processes occurring on a metal surface may sometimes be limited by spin conversion. We present a generic model describing this case. The results obtained are compared with the conventional two-state Landau – Zener model and with a multi-state model implying one-electron transfer between the reactant and the metal. In this context, the specifics of the dissociative adsorption of O_2 on Ag(111) are briefly discussed.

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1. INTRODUCTION

Elementary steps of chemical reactions occurring on a gas–metal interface are of high interest from the standpoints of atomic, molecular, and solid-state physics, surface science, different branches of chemistry, and numerous applications [1]. For the academic society, this interest is related to the complexity of heterogeneous reactions. Compared to the gas- and liquid-phase reactions, the conceptual basis for interpretation of the kinetics of heterogeneous reactions is much richer due to nontrivial features of the reaction dynamics, adsorbate–adsorbate lateral interactions, surface heterogeneity, spontaneous and adsorbate-induced changes in a surface, and/or limited mobility of reactants [2]. The corresponding applications are associated first of all with catalysis, which forms the mainstay of the chemical industry [3].

Mathematically, heterogeneous reactions are described in terms of coverage of a surface by adsorbed particles [4, 5]. The kinetic equations for adsorbate coverages involve rate constants for elementary reaction steps. As is usual in chemistry, an elementary step or process (these terms are used here interchangeably) is identified with the motion of atomic nuclei along the potential energy surface or surfaces repre-

senting the electronic and nuclear-repulsion energy of the system as a function of nuclear coordinates. This concept is based on the Born−Oppenheimer approximation, implying separation of fast motion of electrons and slow motion of nuclei. At thermal conditions, chemical rate processes often occur along the pathways that lead along the lowest potential energy surface from one stable minimum to another. If this potential energy surface is well separated from higher potential energy surfaces such that the transitions to the latter surfaces are negligible, an elementary process is called adiabatic. Nonadiabatic elementary processes include transitions between different potential energy surfaces. In chemistry in general and in heterogeneous catalysis in particular, the majority of practically important elementary rate processes are usually believed to be adiabatic. However, nonadiabatic processes occur as well.

Identification and scrutiny of nonadiabatic rate processes on metal surfaces is one of the central goals of the theory of heterogeneous chemical reactions [6]. At present, the situation in this field is far from clear. Although the breakdowns of the Born−Oppenheimer approximation in reactions on metals are often anticipated and the relevant experimental data appear to be abundant, good specific examples illustrating in detail what may happen are still lacking. Among a few advances in this field, it is appropriate to mention, e.g.,

*E-mail: zhdanov@fy.chalmers.se
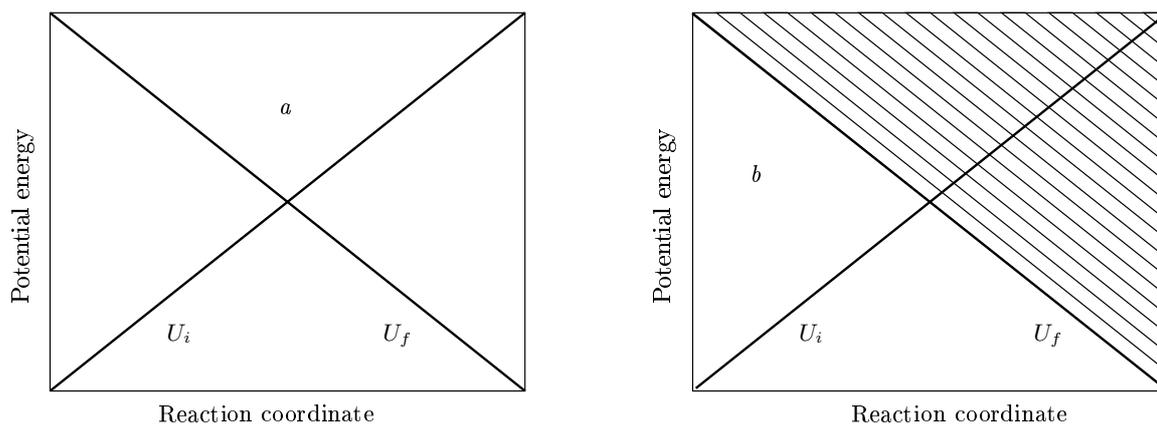
Diabatic potential-energy curves as a function of the reaction coordinate. Panel a corresponds to the conventional two-state Landau–Zener model. Panel b is for the situations where a rate process is limited either by one-electron transfer or by two-electron exchange between the reactants and metal. U_i is the energy of the initial state. U_f is the energy after the electron transfer or electron exchange with participation of metal electrons with the Fermi energy. The thin solid lines correspond to the formation of excited electrons, holes, or electron–hole pairs

direct detection of hot electrons and holes excited by adsorption of atomic H and D on ultrathin Ag and Cu films [7]. In many other cases, the interpretation of experimental data is often far from straightforward. One of the reasons for this situation is that the corresponding general models classifying various scenarios of the dynamics of rate processes are not well developed. Moreover, the conventional software (e.g., the DFT packages) does not allow accurately treating excited states. In this paper, we first briefly recall a few relevant ingredients of the theory of rate processes and then discuss in detail the case of nonadiabatic spin conversion in reactions occurring on a metal surface.

2. GENERAL EQUATIONS

Under thermal conditions, the rates of adiabatic elementary chemical processes can be calculated using the transition-state theory (TST) [8]. According to transition-state theory, the minimum-energy path connecting two stable conformations is identified as the reaction coordinate. The maximum-energy position along the reaction coordinate, representing a saddle point on the potential energy surface, is called the transition (or activated) state. The reaction rate is identified with the reactant flux along the reaction coordinate across the saddle point in the direction of the final conformation. The flux is calculated assuming thermodynamic equilibrium between the activated and initial states.

The rate of nonadiabatic processes is reduced due to the need of jumps from one potential energy surface to another, and therefore the corresponding rate constant is usually represented as

$$k = \kappa k_{TST}, \tag{1}$$

where k_{TST} is the transition-state-theory rate constant and $\kappa \leq 1$ is the so-called transmission coefficient. This coefficient can often be calculated by analyzing the one-dimensional nuclear motion along the reaction coordinate q near the crossing of the diabatic potential energy surfaces (at $q \approx q_0$). According to this approximation, the transmission coefficient is given by

$$\kappa = \frac{\displaystyle\int_0^\infty P(v)f(v)\,dv}{\displaystyle\int_0^\infty f(v)\,dv}, \tag{2}$$

where $P(v)$ is the transition probability, v is the particle velocity at $q = q_0$, and $f(v)$ is the Maxwell velocity distribution.

Near the crossing of the diabatic potential energy curves $U_i(q)$ and $U_f(q)$ (see Figure a), their dependence on the reaction coordinate can often be considered linear. This approximation corresponds to the famous Landau–Zener model [9]. In the most interesting case where the process rate is limited by weak coupling of the diabatic states, this model yields

$$P(v) = \frac{4\pi V^2}{\hbar v F}, \tag{3}$$

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where V is the transition matrix element,

$$F = \left| \frac{\partial U_i}{\partial q} - \frac{\partial U_f}{\partial q} \right|_{q=q_0}$$

is the difference of the potential-energy slopes, and q_0 is the coordinate corresponding to the crossing of the potential energies (we note that this expression for $P(v)$ takes into account that this coordinate is passed two times during the particle motion along $U_i(q)$). The transmission coefficient is accordingly given by

$$\kappa = \frac{(2\pi)^{3/2} m^{1/2} V^2}{\hbar F (k_B T)^{1/2}}, \qquad (4)$$

where m is the particle mass.

The Landau–Zener model is widely used to describe nonadiabatic processes occurring in gas and liquid phases. In the literature, one can also find examples where the conventional version of this model is employed to interpret processes on a metal surface. In that case, the two-state approximation may fail, however, because the electronic states in a metal form a continuum (see Figure b), and the Landau–Zener model should be modified accordingly. The modifications depend on the specifics of reactions. If a rate process is limited by one-electron jumps, e.g., from the states located below the Fermi level in a metal to a vacant adsorbate orbital (this results in the formation of a hole), we have [5]

$$P(v) = \frac{4\pi m v \rho V^2}{\hbar F_i}, \qquad (5)$$

and

$$\kappa = \frac{(2\pi)^{3/2} (m k_B T)^{1/2} \rho V^2}{\hbar F_i}, \qquad (6)$$

where ρ is the density of the electron states and

$$F_i = \left| \frac{\partial U_i}{\partial q} \right|_{q=q_0}$$

is the potential-energy slope.

Here, we treat a more complex situation where a rate process on a metal surface is limited by spin conversion. A likely example of such processes is the dissociative adsorption of O_2. This molecule is well known to be in the triplet state ${}^3\Sigma_g^-$. In particular, the simplest representation for the wave function of two electrons forming this state is [10]

$$\frac{1}{\sqrt{2}} [\pi_{g+}(1)\pi_{g-}(2) - \pi_{g-}(1)\pi_{g+}(2)]\alpha(1)\alpha(2), \qquad (7)$$

where π_{g+}, π_{g-}, and α are the spatial and spin one-electron wave functions. The lowest excited states are the singlets ${}^1\Delta_g$ and ${}^1\Sigma_g^+$. If the O_2–metal interaction is repulsive in the triplet state and attractive in one of the singlet states, the dissociative adsorption of O_2 may be limited by the transition between these states.

To our knowledge, the first attempt to scrutinize the effect of spin conversion on the rate of O_2 adsorption was performed by Kato, Uda, and Terakura [11]. They analyzed O_2 adsorption on Si(001). The triplet–singlet transition was described using the conventional Landau–Zener model. The coupling matrix element V was considered to be related to the spin–orbit interaction. More recently, Behler et al. [12] discussed the influence of the triplet–singlet transition on the rate of O_2 adsorption on Al(111) (for the experiment, see Ref. [13]). Using the DFT packages, the latter authors have illustrated that the existence of the potential barrier for adsorption seems to be related to slow transition between the triplet and singlet states. The dynamics of this transition were not treated explicitly, however.

The spin–orbit interaction is weak, $V \propto 1/c$ (c is the velocity of light). Therefore, the spin conversion in rate processes on a metal surface seems to occur more likely via spin exchange with the metal. In the case of O_2 adsorption, for example, one of the electrons forming the triplet state may jump from the $\pi_g \alpha$ state to a vacant state located above the Fermi level in the metal, and simultaneously an electron with spin β may jump to O_2 from a state located below the Fermi level in the metal.

According to the scenario outlined in the paragraph above, the spin conversion is accompanied by excitation of an electron–hole pair. This means that this process is possible in the region to the right of q_0 (i.e., at $q > q_0$), where $U_i > U_f$ (see Figure b). In this region, the spin-conversion rate can be calculated at a given nuclear coordinate by using the golden rule as

$$r(q) = \frac{2\pi}{\hbar} V^2 \int \rho_\alpha(E_e)\rho_\beta(E_h) \times$$
$$\times \delta[U_i(q) - U_f(q) - E_e - E_h] \, dE_e \, dE_h, \quad (8)$$

where V is the average spin-exchange matrix element, $\rho_\alpha(E_e)$ is the density of vacant electron states with spin α above the Fermi level, $\rho_\beta(E_h)$ is the density of occupied electron states with spin β below the Fermi level, $\delta(E)$ is the delta function, and E_e and E_h are the electron and hole energies defined such that the Fermi energy is equal to zero. Assuming the metal to be nonmagnetic and neglecting the energy dependence of the density of electron states, i.e., using the relation

$$\rho_\alpha(E_e) = \rho_\beta(E_h) = \rho/2,$$

where ρ is the density of states of electrons with both spin directions, we obtain from Eq. (8) that

$$r(q) = \frac{\pi}{2\hbar}\rho^2 V^2 [U_i(q) - U_f(q)]. \tag{9}$$

In the case of weak coupling, the total transition probability is given by integration of $r(q)$ along the particle trajectory determined by the potential $U_i(q)$,

$$P = \int \frac{r(q)\,dq}{v(q)}, \tag{10}$$

where $v(q)$ is the particle velocity. Substituting expression (9) in the integrand and assuming the dependence of U_i on q to be linear, we obtain

$$P(v) = \frac{4m^2 v^3 \rho^2 V^2 F}{3\hbar F_i^2}, \tag{11}$$

where v is the particle velocity at $q = q_0$. Substitution of the last expression in Eq. (2) yields

$$\kappa = \frac{2^{5/2}\pi^{3/2}m^{1/2}(k_B T)^{3/2}\rho^2 V^2 F}{\hbar F_i^2}. \tag{12}$$

3. DISCUSSION AND CONCLUSIONS

Equations (1), (11), and (12) allow one to understand what may happen in the case where a rate process occurring on a metal surface is limited by spin conversion. In particular, Eq. (11) can be used to interpret the molecular-beam experiments performed at a fixed energy of scattering molecules. In the simplest case, the initial kinetic energy E of a molecule and its velocity at $q = q_0$ are related as

$$v = \left[\frac{2(E - \mathcal{E}_a)}{m}\right]^{1/2},$$

where $\mathcal{E}_a \equiv U_i(q_0)$ is the activation barrier. According to Eq. (11),

$$P \propto v^3 \propto (E - \mathcal{E}_a)^{3/2},$$

i.e., the reaction probability rapidly increases with increasing energy. For comparison, it is interesting to note that the conventional Landau–Zener model predicts

$$P \propto \frac{1}{v} \propto \frac{1}{(E - \mathcal{E}_a)^{1/2}}$$

(cf. Eq. (3)), i.e., the reaction probability decreases with increasing energy. For the one-electron transfer, we have

$$P \propto v \propto (E - \mathcal{E}_a)^{1/2}$$

(cf. Eq. (5)), i.e., the reaction probability increases with increasing energy, although much slower compared to Eq. (11).

Equation (12), describing reactions occurring at thermal conditions, indicates that the transmission coefficient may be a few orders of magnitude lower than unity.

Finally, it is instructive to briefly discuss a real process limited by spin conversion. One of the probable candidates is the O_2 adsorption on Ag(111). The molecular-beam experiments [14] indicate that in this case, the dissociation probability rapidly increases with increasing the kinetic energy of O_2 molecules. In particular, the results obtained can be fitted as

$$P \propto (E - \mathcal{E}_a)^{3/2}.$$

An attempt to interpret these results on the basis of a model implying one-electron transfer was performed in Ref. [15]. The one-dimensional version of this model (Eq. (5)) did not allow fitting the experimental data. To reach agreement with the experiment, it was necessary to take the three-dimensional corrections into account. In contrast, the one-dimensional model implying spin conversion (Eq. (11)) makes it possible to describe the experiment. Thus, the rate of O_2 adsorption on Ag(111) is likely to be limited by spin conversion.

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