

The threshold condition is given approximately by $eFd \sim \Delta E$, where d is the period of the superlattice and ΔE is the width of the band where conduction is taking place. The fact that the photocurrents peak at the same voltage for both E_1 and E_2 in Fig. 3 seems to indicate that electrons generated at the higher band relax to the lower one before transport is effected. The asymmetry of the characteristics arises from the presence of the Schottky barrier which shifts the curve toward positive voltages. The shift, as well as the photocurrent levels at forward voltages, however, are found to be somewhat smaller than those expected from a simple Schottky-barrier model. This may be understood on the basis of the field distortion caused by appreciable electron injection at the GaAs-superlattice interface in the forward-bias condition.¹¹

With this consideration, it is possible to compare the observed threshold with that predicted theoretically. Taking into account the barrier height of Au, we find $eFd \sim 10$ meV compared to $\Delta E_1 \sim 7$ meV as calculated for sample B; and ~ 50 meV compared to $\Delta E_1 \sim 38$ meV for sample A. This consistency establishes the effect of quantum states in causing the observed negative differential conductance, and indicates that electrons generated in the conduction band are mainly responsible for the transport properties.

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Friction Coefficient of an Adsorbed H Atom on a Metal Surface*

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The friction coefficient η for a hydrogen adatom on a transition-metal surface is calculated in the spirit of a model proposed by Newns. η shows variation over a wide range of values as the adatom approaches the surface. The implications of our results to catalysis are discussed and related to recent work on the subject.

The problem of a physical approach to catalysis has recently received renewed attention; in particular Suhl and co-workers have emphasized that there is a growing body of experimental evidence that catalytic rates show marked anomalies as a result of phase transitions, alloying, or other causes. In addition, very recent results by Krin-

chik² show a remarkably large amplitude modulation of the catalytic rate of the reaction $\text{Ni} + 4\text{CO} \rightarrow \text{Ni}(\text{CO})_4$ as a function of applied magnetic field intensity. In these cases, small systematic changes of the substrate (for example, varying the temperature across a phase transition) do not change the activation energy significantly, while

the reaction rate κ , given by the reaction-rate equation

$$\kappa = \nu \exp(-F_B/k_B T), \quad (1)$$

changes considerably suggesting a nonconstant prefactor ν . In Eq. (1) T is the temperature, k_B the Boltzmann constant, F_B the barrier free energy, and the prefactor ν is an "attempt" frequency to overcome the barrier.

In this communication we report the results of a first-principles model calculation of the prefactor ν for the adsorption of H on a transition-metal surface. Our model concentrates on the electronic properties of the catalyst and neglects effects due to phonons for the time being; these effects, while relevant in general, are not dominant in the vicinity of the anomalies under consideration. Our results tend to confirm that the reaction rate can vary significantly as a function of the friction parameter η and thus, that absolute rate theory may not always apply, as was already suggested.¹ In Ref. 1 a Brownian-motion model for the interaction between reacting chemicals on metal surfaces and substrate electrons was developed. It was assumed that, even for this quantum mechanical case, the time evolution equation for the distribution function for one-dimensional motion of the adparticle along the reaction path had Fokker-Planck form; the validity and limitations of such a procedure were recently discussed by Schaich.³ A general solution for the Fokker-Planck equation is at present not known, but Kramers⁴ found approximate solutions for the small- and large- η limits, where η is the friction coefficient which describes the interactions of the adparticle with the substrate degrees of freedom, and showed that for a potential barrier of height V_B

$$\kappa \sim \eta \beta V_B \exp(-\beta V_B), \quad \eta < \omega_A / \beta V_B, \quad (2)$$

and

$$\kappa \sim (\omega_A \omega_B / \eta) \exp(-\beta V_B), \quad \eta > \omega_B. \quad (3)$$

Here $\beta^{-1} = k_B T$, V_B is the height of the barrier, and ω_A and ω_B are related to the curvature at the bottom and top of the barrier, respectively, through

$$\omega_{A,B} = (2/M) |\partial^2 V / \partial R^2|_{A,B}.$$

Kramers also presented strong evidence that for intermediate values of η the kinematic theory of Glasstone, Laidler, and Eyring,⁵ known as absolute rate theory (ART), does apply.

In spite of this it is widespread use to assume that the prefactor ν in Eq. (1) is simply constant. In order to explore the possibility that in some catalytic reactions ART may not apply, we have carried out a model calculation of the parameter η for the adsorption of atomic H on a transition-metal surface, in the spirit of the treatment given by Newns.⁶

The formula we have used to obtain η is

$$\eta^{\alpha\delta} = M^{-1} \text{Re} \beta \int_0^\infty d\tau \langle \hat{\mathcal{F}}^\alpha(0) \hat{\mathcal{F}}^\delta(\tau) \rangle, \quad (4)$$

where M is the adparticle mass, $\hat{\mathcal{F}}^\alpha = \hat{F}^\alpha - \langle \hat{F}^\alpha \rangle$, and \hat{F}^α is the α th Cartesian component of the adparticle force operator. Equation (4), which is closely related to well-known force-autocorrelation representations of dissipation coefficients, was derived¹ invoking the large- M limit, on the basis of a bootstrap procedure in which the coefficients of the Fokker-Planck equation were obtained by calculation of physical quantities using this equation and independently, through a rigorous quantum mechanical procedure; finally the results are equated to yield Eq. (4).

As already mentioned above we formulate our model following the scheme of Newns⁶ who studied the analogous chemisorption problem. The Hamiltonian has the form of the one Anderson⁷ used to describe magnetic impurities, that is

$$\mathcal{H} = \sum_{k,\sigma} \epsilon_k c_{k\sigma}^\dagger c_{k\sigma} + \sum_{\sigma} \epsilon_a a_{\sigma}^\dagger a_{\sigma} + (1/\sqrt{N}) \sum_{k,\sigma} (V_{k_a} c_{k\sigma}^\dagger a_{\sigma} + V_{a k} a_{\sigma}^\dagger c_{k\sigma}) + U \hat{n}_{a,\sigma} \hat{n}_{a,-\sigma}. \quad (5)$$

Here $c_{k\sigma}^\dagger$ ($c_{k\sigma}$) and a_{σ}^\dagger (a_{σ}) create (destroy) the set of unperturbed eigenfunctions $|\vec{k}\rangle$ and $|a\rangle$ of the metal and the hydrogen atom, respectively, while σ denotes the electron spin. We limit our basis set to the eigenstates $|\vec{k}\rangle$ of the semi-infinite metal and the hydrogen 1s orbitals, and they are assumed orthogonal to each other. The effect of nonorthogonality enters the calculation of the friction coefficient η only through minor modifications of the Green's functions, which are unimportant for a qualitative discussion.⁸

The adparticle force operator thus takes the form

$$\hat{F} = (1/\sqrt{N}) \sum_{k,\sigma} (\vec{W}_{k_a} c_{k\sigma}^\dagger a_{\sigma} + \vec{W}_{a k} a_{\sigma}^\dagger c_{k\sigma}), \quad (6)$$

where

$$\vec{W}_{\vec{k}a} = - \int \varphi_{\vec{k}}^*(\vec{x}) \nabla \mathcal{H} \varphi_a(\vec{x}) d^3x. \quad (7)$$

Substitution of Eq. (6) in Eq. (4) yields, in Hartree-Fock approximation,

$$\eta^{\alpha\alpha} = (MN)^{-1} \text{Re} \beta \sum_{\vec{k}, \vec{k}'} \int_0^\infty d\tau [W_{\vec{k}a}^{\alpha} W_{a\vec{k}'}^{\alpha} \langle c_{\vec{k}\sigma}^\dagger c_{\vec{k}'\sigma}(\tau) \rangle \langle a_\sigma a_\sigma^\dagger(\tau) \rangle + W_{a\vec{k}'}^{\alpha} W_{\vec{k}a}^{\alpha} \langle c_{\vec{k}\sigma} c_{\vec{k}'\sigma}^\dagger(\tau) \rangle \langle a_\sigma^\dagger a_\sigma(\tau) \rangle + W_{\vec{k}a}^{\alpha} W_{\vec{k}'a}^{\alpha} \langle c_{\vec{k}\sigma}^\dagger a_\sigma(\tau) \rangle \langle a_\sigma c_{\vec{k}'\sigma}^\dagger(\tau) \rangle + W_{a\vec{k}'}^{\alpha} W_{a\vec{k}'}^{\alpha} \langle c_{\vec{k}\sigma} a_\sigma^\dagger(\tau) \rangle \langle a_\sigma^\dagger c_{\vec{k}'\sigma}(\tau) \rangle]. \quad (8)$$

Also within the Hartree-Fock approximation, the Green's functions related to the Hamiltonian of Eq. (5) are easily obtained in closed form; with these Green's functions the correlation functions of Eq. (8) can be evaluated and yield the result

$$\eta^{\alpha\alpha} = \frac{1}{\pi M} \sum_{\sigma} \left[\frac{\mu^{\alpha} \Gamma}{E_{a\sigma}^2 + \Gamma^2} + (\nu^{\alpha})^2 \frac{E_{a\sigma}^2 - \Gamma^2}{(E_{a\sigma}^2 + \Gamma^2)^2} \right], \quad (9)$$

where the parameters Γ , μ^{α} , and ν^{α} were assumed constant. Their definition is

$$\mu^{\alpha} = (-1/N) \text{Im} \sum_{\vec{k}} \vec{k} |W_{\vec{k}a}^{\alpha}|^2 / (\omega_+ - \epsilon_k), \quad (10)$$

$$\nu^{\alpha} = (-1/N) \text{Im} \sum_{\vec{k}} \vec{k} V_{\vec{k}a}^{\alpha} W_{a\vec{k}}^{\alpha} / (\omega_+ - \epsilon_k), \quad (11)$$

$$\Gamma = (-1/N) \text{Im} \sum_{\vec{k}} |V_{\vec{k}a}^{\alpha}|^2 / (\omega_+ - \epsilon_k), \quad (12)$$

with $\omega_+ = \omega + i0^+$ and $E_{a\sigma} = \epsilon_a - \epsilon_F + U \langle n_{a,-\sigma} \rangle$.

In order to carry out a numerical evaluation of η , we have taken μ^{α} , ν^{α} , and Γ as parameters, with the following approximate forms:

$$\mu^{\alpha} = \pi N(0) \langle |W_{\vec{k}a}^{\alpha}|^2 \rangle_{\text{FS}} = \pi N(0) W_{k_{\text{Fa}}}^2, \quad (13)$$

$$\nu^{\alpha} = 0, \quad (14)$$

$$\Gamma = \pi N(0) \langle |V_{\vec{k}a}^{\alpha}|^2 \rangle_{\text{FS}} = \pi N(0) V_{k_{\text{Fa}}}^2, \quad (15)$$

where $N(0)$ is the density of conduction-electron states per spin direction at the Fermi level and $\langle \dots \rangle_{\text{FS}}$ denotes an average over the Fermi surface. For ν^{α} to vanish exactly it is sufficient that the potential which mixes the $|\vec{k}\rangle$ and $|a\rangle$ states and the $|a\rangle$ states themselves be spherically symmetric.

Furthermore, we have assumed that

$$W_{k_{\text{Fa}}} = (\rho/a_0) V_{k_{\text{Fa}}}, \quad (16)$$

where ρ is a dimensionless scaling parameter and a_0 the Bohr radius. With these assumptions it is easy to show that $\eta^{\alpha\alpha}$ scales proportionally to $\rho^2 V_{k_{\text{Fa}}}^2$ and thus only one parameter, which we choose to be $\epsilon_a - \epsilon_F$, is necessary to label the plots of η as functions of Γ which are displayed in Fig. 1. Γ is a measure of the overlap between atomic and substrate states and since this overlap increases as the adatom nears the surface

the plots of η versus Γ give an idea of the variation of the friction coefficient as a hydrogen atom approaches the metal substrate.

In relation to these graphs it is important to notice that (1) the friction coefficient does vary over a wide range of values. (2) For $-1 < (\epsilon_a - \epsilon_F)/U < 0$ the curves for η versus Γ show two clearly distinct regions, depending on whether the H adsorbs in a magnetic (small values of $\pi\Gamma/U$) or a nonmagnetic (large $\pi\Gamma/U$) configuration; as we have used the Hartree-Fock approximation the transition from one regime to the other occurs at

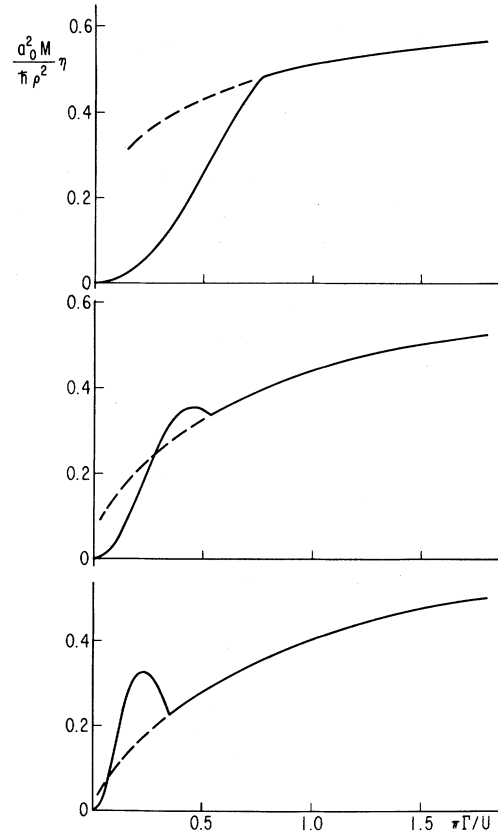


FIG. 1. η versus $\pi\Gamma/U$ with $(\epsilon_a - \epsilon_F)/U = -0.2$ (or 0.8), -0.1 (or -0.9), and -0.05 (or -0.95).

the values calculated by Anderson.⁷ (3) The plots of η versus Γ are the same for $\epsilon_a - \epsilon_F = -0.5U + \Delta$ and $\epsilon_a - \epsilon_F = -0.5U - \Delta$ [i.e., the graphs for $(\epsilon_a - \epsilon_F)/U = -0.75$ and -0.25 are identical].

(4) For large values of $\pi\Gamma/U$ the friction coefficient η tends asymptotically to a constant value (in the abscissa units of our figures this value is $2/\pi$). Thus for strong admixture, or equivalently when the adparticle is very near the substrate surface, the friction smoothly attains a constant value.

In the opposite limit $\eta \rightarrow 0$ as $\pi\Gamma/U \rightarrow 0$ for the stable magnetic and nonmagnetic configurations. For the unstable nonmagnetic configuration (dashed lines in the graphs) η tends to a spurious nonzero value when $\pi\Gamma/U \rightarrow 0$. This behavior of the physically unstable solution could be a consequence of our Hartree-Fock approximation and may disappear in a spin-fluctuation or charge-fluctuation solution; the effect of these fluctuations on the friction, and thus on the reaction rate, could be quite important and deserves further investigation.

It is also interesting to notice that for $(\epsilon_a - \epsilon_F)/U \lesssim 0$ [or equivalently $(\epsilon_a - \epsilon_F)/U \gtrsim -1$] the friction η goes through a maximum, which is larger than the (unstable) nonmagnetic value, as the admixture increases (decreasing distance), as illustrated in our figure.

Our results lend support to the claim¹ that ART may not always govern the rate of catalytic reactions and consequently, depending on the values of Γ and $\epsilon_a - \epsilon_F$, the prefactor ν of Eq. (1) can be a sensitive function of η .

At present we are in the final stages of a cal-

ulation of the friction coefficient η for the significantly more complex case $H_2 \leftrightarrow H + H$, where similar features are observed. We will report our results elsewhere shortly.

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