

Electronic friction and covalent chemisorption

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The energy loss to low-energy electron-hole pairs in the process of sticking at metal surfaces is discussed for atoms or molecules which form a covalent chemisorption bond. Using the Friedel sum rule it is shown that a different symmetry behavior of the highest occupied molecular orbital and the lowest unoccupied molecular orbital is favorable for larger electronic friction.

Two energy-loss mechanisms have been considered in the description of sticking of atoms or molecules at metal surfaces: The excitation of phonons,<sup>1-3</sup> and the energy-loss to low-energy electron-hole (*e-h*) pairs.<sup>4-20</sup> The phonon mechanism is usually assumed to be the more important one. The relative importance of the electronic mechanism, on which we concentrate in the following, is largest for light chemically reactive adsorbates. To simplify the theoretical description, the adsorbate motion is often

treated classically, which turns out not to be a serious approximation.<sup>16</sup> The adsorbate motion then acts as a slowly varying localized time-dependent perturbation on the electronic system, if the adsorbate approaches the surface with "thermal" energy. In previous publications<sup>10,11,18</sup> we have presented a description of the electronic excitations in the spirit of the adiabatic expansion, where the low-lying *e-h* pairs are treated as bosons. For noninteracting electrons, we obtain at  $T = 0$  for the probability density  $P(\epsilon)$  to create excitations with energy  $\epsilon$ ,<sup>10,11</sup>

$$P(\epsilon) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\epsilon t} \exp \left[ - \sum_{\alpha, \alpha'} \int_0^{\infty} \frac{|v_{\alpha\alpha'}(\epsilon')|^2}{\epsilon'} (1 - e^{-\epsilon' t}) d\epsilon' \right], \tag{1}$$

with

$$v_{\alpha\alpha'}(\epsilon) = - \int_{-\infty}^{\infty} \langle \epsilon_F, \alpha | \dot{H}_I | \epsilon_F, \alpha' \rangle^t e^{i\epsilon t} dt. \tag{2}$$

Here the  $|\epsilon_F, \alpha\rangle^t$  are the adiabatic one-particle eigenstates  $H_I |\epsilon, \alpha\rangle^t = \epsilon |\epsilon, \alpha\rangle^t$  at the Fermi energy  $\epsilon_F$ , which are labeled by their energy  $\epsilon$  and additional quantum numbers  $\alpha$ . For the important special case (see below) that the one-particle eigenstates can be chosen in such a way that the perturbation is *diagonal* in the additional quantum numbers  $\alpha$ , the boson assumption can be justified rigorously for slow perturbations in terms of coherent *e-h* pair operators<sup>11,18</sup> (Tomonaga bosons<sup>21</sup>). In the general case the expression (1) for  $P(\epsilon)$  is probably not asymptotically exact for slow perturbations. Without the boson assumption, Eq. (1) can also be derived in a leading-order cumulant expansion in the inelasticity.<sup>9,19</sup>

When the perturbation is diagonal in the  $\alpha$ 's, the coupling matrix elements  $v_{\alpha\alpha'}(\epsilon)$  can be expressed in terms of the instantaneous scattering phase shifts  $\delta_{\epsilon_F, \alpha}(t)$  of the different channels at the Fermi

energy<sup>10,11,13</sup>

$$v_{\alpha\alpha'}(\epsilon) = \delta_{\alpha\alpha'} \int_{-\infty}^{\infty} [\dot{\delta}_{\epsilon_F, \alpha}(t)/\pi] e^{i\epsilon t} dt, \tag{3}$$

and the excitation probability  $P(\epsilon)$  is given as a convolution of the excitation probabilities of the individual channels.

In a very simple description of the interaction between the adsorbate and the substrate only a single adsorbate level is taken into account<sup>8,11</sup>:

$$H_I = \sum_k (\epsilon_k n_k) + \epsilon_a(t) n_a + \sum_k [V_{ak}(t) \psi_a^\dagger \psi_k + \text{H.c.}], \tag{4}$$

where the substrate levels are described by  $\epsilon_k$ ,  $k$  labeling the wave vector  $\bar{k}$  and the band index  $n$ , the adsorbate level by  $\epsilon_a(t)$ , and  $V_{ak}(t)$  gives the interaction between the two systems. The description simplifies considerably, when the interaction is with the *same* local metal state all the time, and only the interaction strength varies with time, i.e.,  $V_{ak}(t)$

$= V(t)A_k$ . Then the perturbation presented by the adsorbate couples only to a one-dimensional subspace of metal states defined by

$$|\epsilon\rangle = \sum_{n, \vec{k}} A_{\vec{k}, n} \delta(\epsilon - \epsilon_{\vec{k}, n}) |\vec{k}, n\rangle, \quad (5)$$

and the interaction can be described by a *single* phase shift<sup>11</sup>  $\delta_{\epsilon_F}(t)$  [with  $V(t) = (\sum_k |V_{ak}(t)|^2)^{1/2}$ ],

$$\begin{aligned} \dot{\delta}_{\epsilon_F}(t) = & -\pi \{\dot{\epsilon}_a(t) \\ & + 2[\epsilon_F - \epsilon_a(t)] \dot{V}(t)/V(t)\} \rho_a'(\epsilon_F), \end{aligned} \quad (6)$$

where  $\rho_a'(\epsilon)$  is the adsorbate density of states given by

$$\rho_a'(\epsilon) = \pi^{-1} \text{Im} \{ [\epsilon - \epsilon_a(t) - \Gamma_t(\epsilon - i0)]^{-1} \}, \quad (7)$$

with

$$\Gamma_t(z) = \sum_k \frac{|V_{ak}(t)|^2}{z - \epsilon_k}.$$

The simple model (4) has been used to describe adsorbates with an affinity level that crosses the Fermi level while approaching the surface.<sup>11</sup> Such a crossing can lead to a large inelasticity when the “crossing time” is short compared to the “round trip” time in the adsorption well.<sup>8, 11, 14</sup>

If one uses a simple model of noninteracting electrons like in (4), and nevertheless wants to get the overall screening properties right, one has to impose a constraint on the parameters of the perturbation such that the Friedel sum rule<sup>22</sup> (FSR) is fulfilled. For the chemisorption of a neutral atom or molecule this means that the total number of locally displaced electrons has to vanish:

$$\text{Im Tr} \ln [1 - G_0(\epsilon_F - i0) V_t] = 0, \quad (8)$$

where  $G_0(z) = (z - H_0)^{-1}$ . Obviously, we cannot fulfill the FSR and have energy dissipation in the single-level model, because (8) just leads to

$$\mu_1 = 2\pi \int_{-\infty}^{\infty} [(\dot{\delta}_1)^2 + (\dot{\delta}_2)^2 + 2\dot{\delta}_1 \dot{\delta}_2 \rho_{a_1 a_2}' \rho_{a_2 a_1}' / (\rho_{a_1 a_1}' \rho_{a_2 a_2}')] dt, \quad (12)$$

with

$$\dot{\delta}_i = -[\dot{\epsilon}_{a_i} + 2(\epsilon_F - \epsilon_{a_i}) \dot{V}_i/V_i] \rho_{a_i a_i}', \quad (13)$$

and

$$\rho_{a_i a_j}' = \pi^{-1} \text{Im} \{ [\epsilon_F - \hat{\epsilon}_a(t) - \hat{\Gamma}_t(\epsilon_F - i0)]^{-1} \}_{ij}, \quad (14)$$

where  $\hat{\epsilon}_a(t)$  is the  $2 \times 2$  diagonal matrix describing the adsorbate levels and the matrix  $\hat{\Gamma}_t$  describes the

$\dot{\delta}_{\epsilon_F}(t) \equiv 0$  for all times. A known way out of this dilemma is the following argument<sup>6</sup>: If one takes into account the (small) variation of the energy levels of the metal atoms close to the adsorbate, this leads to a “several channel” problem with, again, the one phase shift due to the adsorbate level being large and a large number ( $N$ ) of small additional phase shifts  $\sim 1/N$  which allow one to fulfill the FSR. But, as the *square* of the phase shifts enter the expression for the energy dissipation, these additional phase shifts lead to a contribution  $\sim N(1/N)^2 \sim 1/N$  which can be neglected.

In the following we want to describe the case of covalent chemisorption using two adsorbate levels: The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). In that case we can fulfill the FSR without an “additional phase-shifts” assumption and study its consequences. The Hamiltonian now reads

$$\begin{aligned} H_t = & \sum_{k, \sigma} \epsilon_k n_{k\sigma} + \sum_{i=1,2; \sigma} \epsilon_{a_i}(t) n_{a_i \sigma} + \sum_{i=1,2; \sigma} V_i(t) \psi_{a_i \sigma}^\dagger \psi_{b_i \sigma} \\ = & \text{H.c.}, \end{aligned} \quad (9)$$

where  $\psi_{b_i \sigma}^\dagger$  is the creation operator of the normalized one-particle state

$$|b_i\rangle = \sum_k A_{ki} |k\rangle, \quad (10)$$

with spin  $\sigma$ . Without additional assumptions about the  $A_{ki}$  (see below) it is difficult to evaluate the expression (1) for  $P(\epsilon)$ . We therefore discuss only the first moment  $\mu_1$  of  $P(\epsilon)$  which gives the average energy transfer:

$$\mu_1 = \pi \int_{-\infty}^{\infty} \text{Tr}(\hat{\rho} \dot{H}_t \hat{\rho} \dot{H}_t) dt, \quad (11)$$

with  $\hat{\rho} = \delta(\epsilon_F - H_t)$ . The integrand is closely related to the friction coefficient.<sup>4</sup> Evaluation of the trace using (9) and the equations of motion to express  $\underline{b}$ -matrix elements of  $\hat{\rho}$  in terms of  $\underline{a}$ -matrix elements leads to

coupling to the metal substrate

$$[\hat{\Gamma}_t(z)]_{ij} = V_i(t) V_j(t) \langle b_i | (z - H_M)^{-1} | b_j \rangle. \quad (15)$$

Here  $H_M$  is the first term in (9) which describes the unperturbed substrate. The FSR for the two-adsorbate level case can be written after differentiating (8) with respect to time as

$$\text{Tr}(\hat{\rho} \dot{H}_t) = 2(\dot{\delta}_1 + \dot{\delta}_2) = 0. \quad (16)$$

Therefore one of the phase shifts can be eliminated in Eq. (12). There are two extreme cases in which our result (12) for the average energy transfer simplifies further:

(a) For  $|b_1\rangle = |b_2\rangle$ , i.e., if the HOMO and the LUMO couple to the same localized metal state one obtains from Eq. (14) that  $\rho_{a_1 a_2} \rho_{a_2 a_1} = \rho_{a_1 a_1} \rho_{a_2 a_2}$ . Together with the FSR Eq. (16), this leads to

$$\mu_1 = 2\pi \int (\dot{\delta}_1 + \dot{\delta}_2)^2 dt = 0, \quad (17)$$

i.e., without an (*ad hoc*) additional phase-shifts assumption there is no electronic energy dissipation.

(b) If the off-diagonal terms  $\Gamma_{12}$  vanish identically, i.e.,  $\langle b_1 | \delta(\epsilon - H_M) | b_2 \rangle = 0$ , the off-diagonal terms  $\rho_{a_1 a_2}$  also vanish and we obtain

$$\mu_1 = 2\pi \int [(\dot{\delta}_1)^2 + (\dot{\delta}_2)^2] dt = 4\pi \int (\dot{\delta}_1)^2 dt. \quad (18)$$

This is the "independent channel" case, and the exact expression for  $P(\epsilon)$  is given by Eq. (1) with the simplification Eq. (3).

If there is a symmetry operation  $\hat{T}$  for the unperturbed substrate, i.e.,  $[H_M, \hat{T}] = 0$ , we can classify the unperturbed one-particle eigenstates according to the energy  $\epsilon$ , the eigenvalues  $t_n$  of  $\hat{T}$ , and additional quantum numbers  $\mu$ :

$$\langle b_1 | \delta(\epsilon - H_M) | b_2 \rangle = \sum_{t_n, \mu} \langle b_1 | \epsilon, t_n, \mu \rangle \langle \epsilon, t_n, \mu | b_2 \rangle. \quad (19)$$

If now the  $|b_i\rangle$  are also eigenstates of  $\hat{T}$  with different eigenvalues, then the off-diagonal density of states  $\rho_{b_1 b_2}$  vanishes identically and case (b) results. We therefore come to the conclusion that the HOMO and the LUMO have to couple to metal states of "different symmetry" to obtain a large electronic friction.

As an example, we consider the adsorption of CO and assume that the CO molecule approaches the surface with the molecular axis perpendicular to the metal surface. The  $5\sigma$  orbital (HOMO) and the  $2\pi$  orbital (LUMO) have different symmetry with respect to a  $180^\circ$  rotation around the molecular axis. If the CO adsorbs in a site for which a  $180^\circ$  rotation about the perpendicular axis is a symmetry operation for the substrate we have case (b) and therefore can expect a non-negligible electronic friction. If the molecule approaches the surface with a different orientation of the molecular axis one has to evaluate the general expression of Eq. (12).

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