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Effect of electronic relaxation on covalent adsorption reaction rates

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We present a theory of the effects of intra- and extra-adsorbate electronic response on the dynamics of unimolecular covalent chemisorption on solid surfaces. Our point of departure is the description of the rate processes in terms of diabatic transitions developed by Gadzuk and Metiu and applied to the problem of ionic chemisorption. In this case, the diabatic transitions are characterized by the transient ionization of reactants and a consecutive dynamic response of the substrate electronic degrees of freedom to the perturbation brought about by the ionization of the adsorbate. In covalent chemisorption, however, the adsorbate-induced resonances may form at the Fermi level, leaving the products neutral, so that only spatial rearrangement of the charge around the adsorbate is permitted in a diabatic transition. This situation requires a supplementary treatment since in such a case the electronic relaxation will proceed through two distinct channels, viz., one involving the substrate conduction-band states and the other involving localized adsorbate-induced resonance states. In this paper we investigate the consequences of the interplay between these two types of relaxation processes on the reaction rates pertinent to covalent chemisorption. We find that it gives rise to qualitatively new features in the diabatic transition probability, which differ radically from the x-ray-edge—type effects encountered in ionic chemisorption. The estimate of the effectiveness of the irreversible coupling of the nuclear motion of the incident beam of particles to this relaxation mechanism shows that the inelastic energy transfer through the two channels involved may be of the order of thermal energies for a typical covalent adsorption system.

I. INTRODUCTION

Quantal studies of rate processes in unimolecular adsorption on metal surfaces usually involve two distinct types of energy-transfer mechanisms: (i) inelastic excitations of phonons, and (ii) substrate electron-hole (e-h) pairs. The effect of phonons on atom-surface collisions,[1] desorption,[2] vibrational line shapes of adsorbed molecules,[3] and surface reactions[4] has been discussed extensively by several authors. Despite the fact that the role of e-h pairs as a dissipative mechanism in time-dependent particle interactions with surfaces was pointed out more than a decade ago[5] and used in explanations of adsorbate spectral properties,[6,7] comparatively little attention has been paid to this channel of energy transfer in surface collisions.[8–10] However, in chemical reactions which involve a nonadiabatic change of the electronic configuration of both the adsorbate and the substrate, including a possible charge transfer, the effect of the electronic relaxation in the two subsystems cannot be neglected.

Gadzuk and Metiu[9] developed a theory of rate processes at surfaces in which a close analogy was made between the inelastic processes in unimolecular adsorption and the so called *x-ray-edge effects* characteristic of the adsorption spectra of core levels in solids[11–13] and adsorbates.[6,7] The basic premises of this theory are the following: Interactions of atoms (molecules) moving with thermal energies in the vicinity of a metal surface may be described in terms of nonadiabatic (or diabatic) energy curves describing the potential acting between the surface and the atom in the initial, reactant state and in the final, product state.[9,10,14] The chemical rearrangement of the atom and substrate valence orbitals in a collision of the atom with the surface proceeds in a nonadiabatic fashion even within the Born-Oppenheimer approximation (BOA). This rearrangement of the electronic structure of the system occurs at a characteristic distance $\vec{R}_c$ at which the two diabatic curves intersect. The change of the electronic structure of the adatom from a reactant to the product state may result in the ionization of the latter, whose effective charge appears as a sudden localized perturbation on the electrons in the metal surface. At this point a close analogy with the x-ray-edge effect becomes possible. It was known from the earlier works of Mahan,[15] Anderson,[11] Nozières and co-workers,[12] and Müller-Hartman, Ramakrishnan, and Toulouse[5] that a localized time-dependent perturbation could induce excitation of a large number of e-h pairs in a Fermi sea at a very low energy expense, leading to an infrared divergence in the absorption spectrum of the system. Simple analysis showed that the probability of such a singular many-body relaxation process may be large under usual circumstances.[13] The next step was to calculate these inelastic absorption spectra from the parameters characterizing the adsorption events and to correlate them with the kinetic-energy losses of the adsorbing particles. Using the surface-response formalism of Gumhalter and Newns,[6] Gadzuk and Metiu[9] were able to show that, provided a sufficient amount of the particle initial kinetic energy was transferred to the substrate e-h excitations, the particle would remain trapped in the potential well of the product state and, hence, attached to the surface.

The above description rests on the assumption of a transition of the adatom (molecule) electronic structure from a homopolar to an ionic state at the distance $\vec{R}_c$ from the surface. The probability of this transition is determined by the chemistry of the problem and should be calculated along lines similar to the ones followed in the problems of predissociation[16–18] and nonradiative transitions in diatomic molecules[19–21] bound by an ionic bond. Typical simple examples are molecules of alkali halides for which the change from homopolar to ionic character is very sudden and occurs at relatively large nuclear separations, usually of the order of 10 Å.[20]

The theory of Gadzuk and Metiu[9] should be applicable to the case of ionic chemisorption for which, in the vicinity of the crossing of the diabatic curves, the product-state atomic orbitals develop into resonances located primarily *above* or *below* the Fermi level of the substrate. Only in this case will the charge transfer from one electronic subsystem to the other give rise to the occurrence of the ionic potential causing the inelastic excitation of the *e-h* pairs and the subsequent adatom kinetic-energy dissipation through this channel. This process may, in simple terms, be visualized as a response of a set of harmonic oscillators to the perturbation brought about by the diabatic ionization of the adsorbing atom. Now, the question arises whether in homopolar or covalent chemisorption, i.e., in the case where at the crossing point $\vec{R}=\vec{R}_c$ the two electronic subsystems undergo only a sudden charge rearrangement rather than ionization, is the same concept of relaxation and energy transfer through the Fermi-sea fluctuations applicable. In other words, we are interested in whether the *e-h* excitations may also represent an efficient inelastic mechanism required for dissipation of the adatom kinetic energy in atom-surface collisions characterized by predissociation behavior originating from covalent bonding.

The purpose of the present paper is to supplement the earlier studies of the mechanism of the electronic relaxation by extending it to the case which may occur in the rate processes pertinent to covalent-bond formation in the product states. The systems on which we focus our attention are those in which (i) the adsorbate valence resonances, which at $\vec{R}=\vec{R}_c$ form out of the discrete atomic orbitals, are located around the Fermi level of the substrate, and (ii) the electronic occupation of these resonances does not vary appreciably as the adsorbate moves from the intersection $\vec{R}_c$ of the diabatic curves into the final relaxed state. This is a situation opposite to the one studied in Ref. 9. Speaking again in simple terms, this may be visualized as a response of two sets of coupled oscillators, one representing the substrate and the other the adsorbate, to a sudden displacement from their equilibrium position caused by bonding. We shall show below that mutually coupled electronic relaxation processes in the substrate and within the adsorbate resonance, which are induced by diabatic crossing, may also open an inelastic channel for energy transfer in the atom-surface collisions. However, due to the enhanced phase space for relaxation, its dynamic features will differ strongly from the ones encountered in ionic chemisorption. Ultimately, they will lead to fundamentally different properties of the inelastic spectrum, such as the appearance of the no-loss line, the dependence of the transition rates on the adatom resonance density of states, etc., all of which were not present in the complementary problem of ionic chemisorption.

In Sec. II we present the model for description of the rate of transition of the system from the initial state in which the atom (molecule) is moving towards the surface, into a final state in which it is bound to the surface by a covalent bond. The Born-Oppenheimer, Franck-Condon, and weak-overlap approximations are used to simplify the expressions for the transition rate and bring it to the form amenable to a time-dependent treatment. In Sec. III we define the time correlation function corresponding to the transition rate and introduce the electronic charge-density fluctuations pertaining to the system characterized by a covalent bond between the adatom and the metal in the final, product state. The time-dependent treatment of the coupled charge-density fluctuations leads then to an expression for the transition rate in terms of the convolution of the adatom and the substrate electronic density-density correlation functions. The resulting loss spectrum is shown to exhibit properties which differ from those found by Gadzuk and Metiu[9] for ionic chemisorption. The physical mechanism underlying these differences is discussed and explained in terms of time-dependent perturbations acting on the Fermi sea of the composite system. We apply the results of our study to estimate the average energy loss likely to occur in covalent chemisorption. For a reasonable choice of quantities describing the adsorption event we show that the average energy loss due to electronic excitation, when compared with the initial kinetic energy of a thermalized particle, may represent an efficient inelastic scattering mechanism. Moreover, its magnitude turns out to be of the same order as the one characteristic of ionic chemisorption for the same parameters typifying the substrate free-electron properties.

II. DIABATIC TRANSITIONS AND REACTION RATES

A. Diabatic states in atom-surface reactions

A description of the interactions of atoms and molecules with solid surfaces usually starts with a definition of a Hamiltonian H of the system which is comprised of nuclear and electronic kinetic energies, the electronic interactions with nuclei and among themselves, and the interaction among the nuclei. The conventional division of the Hamiltonian is made into the terms corresponding to the nuclear kinetic energy and the remainder which collects all the other interactions,

$$H=T+H_{\text{el}} . \tag{1}$$

Here T is the kinetic-energy operator of all the nuclei. Since in the following we are going to deal only with the electronic excitations and their effect on the transition rates, we shall henceforth neglect the nuclear motion of the ions in the metal. This reduces T to the kinetic-energy operator of the incoming atom (molecule). Introducing the electronic density operator $\rho(\vec{r})$ we may write H_{el}, in the case of a single atom interacting with the surface, as

$$\begin{aligned} H_{\text{el}} = H_{\text{el}}^{\text{kin}} &+ \tfrac{1}{2}\int d^3r' \int d^3r'' \frac{\rho(\vec{r}\,')\rho(\vec{r}\,'')}{|\vec{r}\,'-\vec{r}\,''|} \\ &- \int d^3r' \frac{Z_m \rho(\vec{r}\,')}{|\vec{r}\,'-\vec{R}_m|} - \sum_j \int d^3r' \frac{Z_j(\vec{r}\,')}{|\vec{r}\,'-\vec{R}_j|} \\ &+ \sum_j \frac{Z_m Z_j}{|\vec{R}_m-\vec{R}_j|} , \end{aligned} \qquad (2)$$

where $\vec{R}_m$ and $\vec{R}_j$ denote the radius vectors of the nuclei of the incoming atom and the jth metal ion, respectively, and the Z's are the corresponding nuclear charges.

The eigenfunctions of the Hamiltonian (1) may be calculated by making use of the several approximations among which the BOA is the most common. The application of the BOA, in which the effect of the nuclear motion on the highly mobile electrons is neglected, may lead to the definition of the *adiabatic* states which are the eigenstates of H_{el}. The adiabatic potential curves are the corresponding eigenvalues of H_{el} calculated for each atom-surface separation $\vec{R}$. This approach to atom-surface reactions, in which the deviations from the BOA give rise to reaction rates, has been pursued by Brivio and Grimley.[8]

However, as pointed out by O'Malley,[18] the experimental evidence shows that the dynamics of the reacting systems does not proceed smoothly along the adiabatic curves, but rather nonadiabatically along the sets of diabatic states which describe the essential properties of the reactants and products separately. The reaction process may be viewed as a transition from the diabatic (electronic) state of the reactants to that of the products. In a simple case of a diatomic molecule, the essential features characterizing such a diabatic transition were calculated by Landau[16] and Zener[17] more than half a century ago.

In the present treatment we shall follow the formulation of diabatic transitions in atom-surface reactions given by Metiu and Gadzuk[10] (MG), which we will recall briefly. We assume that two subspaces of electronic wave functions of the system exist, the states of reactants and the states of products. The former set does not allow bonding of the atom to the metal, whereas the latter consists of the states in which a chemical bond is formed between the adatom and the substrate. These states depend on the atom-nucleus—surface separation and are not the eigenfunctions of the H_{el} but rather of its projections onto the subspace of initial (reactant) and final (product) states. To fix the notation we shall denote these wave functions by $\phi_i(\vec{r},\vec{R})$ and $\phi_f(\vec{r},\vec{R})$, respectively. Hence,[10]

$$H_{\text{el}}^{i}\phi_i(\vec{r},\vec{R}) = V_i(\vec{R})\phi_i(\vec{r},\vec{R}) , \qquad (3a)$$

$$H_{\text{el}}^{f}\phi_f(\vec{r},\vec{R}) = V_f(\vec{R})\phi_f(\vec{r},\vec{R}) , \qquad (3b)$$

where H_{el}^{i} and H_{el}^{f} denote the projection of H_{el} onto the subspaces of reactant and product states, respectively, and V_i and V_f denote the potentials on the adatom nucleus in the respective states. A qualitative behavior of $V_i(\vec{R})$ and $V_f(\vec{R})$ is shown in Fig. 1.

For later convenience we may define, with the help of the final-state electronic functions $|f\rangle$, the orthogonal projection operators

$$Q = \sum_f |f\rangle\langle f| \qquad (4a)$$

and

$$P = 1 - Q \qquad (4b)$$

in the subspace of the product (final) states. As pointed out by O'Malley,[21] in some specific situations, which we are also going to consider below (Sec. II D), the states $|f\rangle$ may be assumed to be resonances of finite width. With these definitions the full final-state Hamiltonian and the full final-state wave function satisfy

$$QHQ\Phi_Q(\vec{r},\vec{R}) = E\Phi_Q(\vec{r},\vec{R}), \quad Q\Phi_Q = \Phi_Q \qquad (5)$$

where H is the total Hamiltonian (1). Introducing the quantum numbers α and β for motion of the atoms nucleus in the potentials $V_i(\vec{R})$ and $V_f(\vec{R})$, respectively, we may write, within the BOA, for the initial- and final-state wave functions of the atom,

$$\Phi_{\alpha,i} = ||\alpha,i\rangle\rangle \; |i\rangle , \qquad (6a)$$

$$\Phi_{\beta,f} = ||\beta,f\rangle\rangle \; |f\rangle , \qquad (6b)$$

where the double (single) angular brackets are used for the nuclear (electronic) wave functions. Hence, the adatom nuclear motion in the initial and final states is governed, within the BOA, by the Schrödinger equations

$$H^i(\vec{R})||\alpha,i\rangle\rangle = [T + V_i(\vec{R})]||\alpha,i\rangle\rangle = E_{\alpha i}||\alpha,i\rangle\rangle , \qquad (7a)$$

$$H^f(\vec{R})||\beta,f\rangle\rangle = [T + V_f(\vec{R})]||\beta,f\rangle\rangle = E_{\beta f}||\beta,f\rangle\rangle , \qquad (7b)$$

where

$$V_l(\vec{R}) = \langle l\,|H_{\text{el}}^{l}|\,l\rangle, \quad l = i,f \qquad (7c)$$

is the initial- (i) and final- (f) state potential acting on the atom nuclear motion.

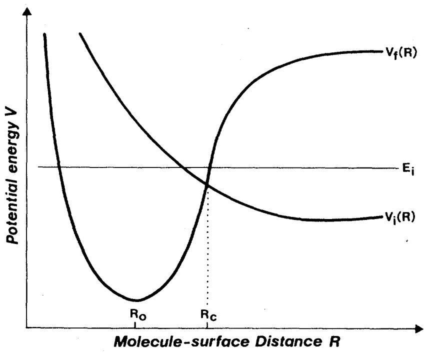

FIG. 1. Schematic diagram of the diabatic potential-energy curves as function of the distance normal to the surface. V_i and V_f denote the initial and final potentials of (7a) and (7b), respectively. E_i is the incident energy of the adsorbate.

B. Reaction probability

In studying the rate processes at surfaces, one is interested in the reaction probability, i.e., the probability that an atom, after having collided with the surface remains in a product state bound to the surface. This requires that part of the atom initial kinetic energy be transferred to the internal degrees of freedom characteristic of the system in the product state. In the present case, these will be the low-energy electronic density fluctuations, whose excitation follows the nonadiabatic transition of the system from the reactant to the product diabatic curve. We assume that the initial state of the system is characterized by the nonbonding ground-state electronic configuration of both the atom and the metal and the nuclear kinetic energy $E_{\alpha,i}$, of the order of thermal energies satisfying $E_{\alpha,i} > \lim V_i(\vec{\mathrm{R}})$ for $R \rightarrow \infty$. The final state of the system consists of a product electronic configuration, in the subspace spanned by Q, and nuclear motion described by a quantum number β and the energy $E_{\beta,f}$, which proceeds along the potential-energy curve $V_f(\vec{\mathrm{R}})$. The transition probability amplitude for such an initial-state—final-state transition is given by[22]

$$T_{\alpha i \rightarrow \beta f} = \int d^3R\, \psi_{\beta f}^{(+)*}(\vec{\mathrm{R}}) \left[\int d^3r\, \phi_f^*(\vec{\mathrm{r}},\vec{\mathrm{R}}) H_{\mathrm{el}}(\vec{\mathrm{r}},\vec{\mathrm{R}}) \times \phi_i(\vec{\mathrm{r}},\vec{\mathrm{R}}) \right] \psi_{\alpha i}(\vec{\mathrm{R}}) \tag{8}$$

where $\phi_i(\vec{\mathrm{r}},\vec{\mathrm{R}}) = \langle \vec{\mathrm{r}} \,|\, i \rangle$, $\phi_f(\vec{\mathrm{r}},\vec{\mathrm{R}}) = \langle \vec{\mathrm{r}} \,|\, f \rangle$, $\psi_{\alpha i}(\vec{\mathrm{R}}) = \langle\!\langle \vec{\mathrm{R}} \,||\, \alpha i \rangle\!\rangle$; and $\psi_{\beta f}^{+}(\vec{\mathrm{R}}) = \langle\!\langle \vec{\mathrm{R}} \,||\, \bar{\beta} \bar{f} \rangle\!\rangle$ satisfies the scattering equation typical of predissociation types of collisions,

$$\{E_{\beta f} - T - [V_f(\vec{\mathrm{R}}) + F_f(\vec{\mathrm{R}})]\} \psi_{\beta f}^{(+)}(\vec{\mathrm{R}}) = 0 \,, \tag{9}$$

with a complex level shift

$$F_f(\vec{\mathrm{R}}) = \int d^3r\, \phi_f(\vec{\mathrm{r}},\vec{\mathrm{R}}) QHP(PE - PHP)^{-1} PHQ \phi_f(\vec{\mathrm{r}},\vec{\mathrm{R}}) \,. \tag{10}$$

For details and interpretation of these terms, see the discussion in Ref. 10, Secs. III B and III C. The wave functions in (8) are subject to the BOA through (7) and (9).

The probability per unit time that the incoming atom ends up in any final product state is

$$P_{\alpha i} = \frac{2\pi}{\hbar} \sum_{\beta f} |\, T_{\alpha i \rightarrow \beta f} \,|^2 \delta((E_{\alpha i} - E_{\beta f}) - (\epsilon_f - \epsilon_i)) \,, \tag{11}$$

where ϵ_i and ϵ_f are the energies of the electronic system in the initial and final state, respectively. The expression (11) can be brought to the standard form of the time correlation function by making use of the integral representation of the δ function. Taking into account the definition of Q, we obtain

$$P_{\alpha i} = \frac{1}{\hbar^2} \sum_{\beta f} \int_{-\infty}^{\infty} dt\, \langle i \,|\, \langle\!\langle \alpha,i \,||\, H_{\mathrm{el}}(\vec{\mathrm{R}}) \,||\, \beta,f \rangle\!\rangle \,|\, f \rangle \times \langle f \,|\, \langle\!\langle \beta,f \,||\, e^{i[T + V_f(\vec{\mathrm{R}}) + H_{\mathrm{el}}^{f}(\vec{\mathrm{R}})]t} H_{\mathrm{el}}(\vec{\mathrm{R}}) e^{-i[T + V_i(\vec{\mathrm{R}}) + H_{\mathrm{el}}^{i}(\vec{\mathrm{R}})]t} \,||\, \alpha,i \rangle\!\rangle \,|\, i \rangle \,. \tag{12}$$

The BOA enables us to commute $T + V_f(\vec{\mathrm{R}})$ with $H_{\mathrm{el}}(\vec{\mathrm{R}})$ and hence

$$P_{i\alpha} = \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt\, \langle i \,|\, \langle\!\langle \alpha,i \,||\, e^{i[V_f(\vec{\mathrm{R}}) - V_i(\vec{\mathrm{R}})]t} H_{\mathrm{el}}(\vec{\mathrm{R}}) Q e^{iH_{\mathrm{el}}(\vec{\mathrm{R}})t} Q H_{\mathrm{el}}(\vec{\mathrm{R}}) e^{-iH_{\mathrm{el}}^{i}(\vec{\mathrm{R}})t} \,||\, \alpha,i \rangle\!\rangle \,|\, i \rangle \,. \tag{13}$$

The explicit double appearance of the projector Q in (13) has been introduced for later convenience. However, in spite of the use of the BOA, expression (13) is still very complicated and calls for the introduction of further simplifying approximations.

C. Franck-Condon approximation

In atom-surface collisions where the energy of the incoming atom $E_{\alpha i}$ is lower than the energy of the crossing point of the two diabatic curves, the reaction probability will be rather small, because of the small overlap between the initial and final nuclear state wave functions. The overlap will increase substantially when the energy is above the crossing point, but not exceeding it too much. For very large $E_{\alpha i}$ the corresponding nuclear wave function will oscillate very rapidly, making the overlap small again. In the interval of energies for which the overlap is appreciable, the nuclear coordinate will be close to $\vec{\mathrm{R}}_c$, and we may approximate all the matrix elements in (13) by their values for $\vec{\mathrm{R}} = \vec{\mathrm{R}}_c$.[16] This gives, for the scattering amplitude into each channel (β,f),

$$T_{\alpha i \rightarrow \beta f} \simeq \langle\!\langle \overline{\beta,f} \,||\, \alpha,i \rangle\!\rangle \int d^3r\, \phi_f^*(\vec{\mathrm{r}},\vec{\mathrm{R}}_c) \times H_{\mathrm{el}}(\vec{\mathrm{r}},\vec{\mathrm{R}}_c) \phi_i(\vec{\mathrm{r}},\vec{\mathrm{R}}_c) \,, \tag{14a}$$

where the term $\langle\!\langle \overline{\beta,f} \,||\, \alpha,i \rangle\!\rangle$ in front of the integral over the electronic coordinates is the Franck-Condon factor between the initial and final nuclear states. The expression (14) contains the essence of the Franck-Condon approximation (FCA). Now, it is seen from (14a) that the driving force for the quantum transition of the adatom nuclear motion from the initial to the final diabatic state in Eqs. (7a) and (7b) is provided by the matrix element

$$V_{fi}(\vec{\mathrm{R}}_c) = \langle f \,|\, H_{\mathrm{el}}(\vec{\mathrm{R}}_c) \,|\, i \rangle = \int d^3r\, \phi_f^*(\vec{\mathrm{r}},\vec{\mathrm{R}}_c) H_{\mathrm{el}}(\vec{\mathrm{r}},\vec{\mathrm{R}}_c) \phi_i(\vec{\mathrm{r}},\vec{\mathrm{R}}_c) \,. \tag{14b}$$

D. Weak-overlap approximation

The Born-Oppenheimer and Franck-Condon approximations used in the derivation of (14) are both reasonably good and are quite common in the studies of molecules and solids. Their use should not introduce any drastic differences between the conclusions about the dynamics of chemical reactions derived either from (8) or (14). To make further progress we introduce the weak-overlap approximation (WOA) in which one assumes that, in the treatment of dynamics of the system in each diabatic state, the electronic wave functions may be represented, to a good approximation, by a product of metal and atomic wave functions. Although this is an obvious choice to represent the reactant wave functions, it may be less justified in the case of products. However, this approximation is extensively used in the studies of chemical-reaction rates[23] and we shall also employ it here in the representation of the product states. This allows the basic features of the transition rates to be calculated. Next, we shall assume that the low-energy electronic density excitations in the system do not affect the existence of the chemical bond in the product state very much. In other words, we assume that the fluctuations of the electronic charge density are characterized by intraband transitions within the metal and transitions within the adsorbate-induced localized resonances where they can take place once the final chemical structure has been established, i.e., after the passage from one diabatic curve to the other. The electronic states may then be written as

$$|i\rangle = |i,O_M\rangle\,|i,o_m\rangle \; , \tag{15a}$$

$$|f\rangle = |f,\Lambda_M\rangle\,|f,\lambda_m\rangle \; , \tag{15b}$$

where i and f on the right-hand side (rhs) of both (15a) and (15b) denote a particular chemical configuration. The quantum numbers O_M,Λ_M, and o_m,λ_m denote the electronic ground state and low excitation modes within the metal (M) and adatom (m) electronic configurations, respectively. (Without introducing any confusion we shall, in the following, omit the subscripts M and m.) The metal initial ground state $|i,0\rangle$ is represented by its unperturbed Fermi-sea continuum, and the atom by its ground-state atomic configuration consisting of the discrete valence orbital states. On the other hand, in the final state, due to the occurrence of a chemical bond between the metal and the adsorbate, the valence orbitals of the atom will broaden into resonances. In the case of covalent-bond formation, these may be only partly occupied. The finite width of a resonance may allow for the intraorbital electronic relaxations[7(a)] in addition to those taking place in the metal states around the Fermi level.[6,9] At this point, our approach goes beyond that of Gadzuk and Metiu,[9] who take into account only the relaxation within the metal states. For this reason their model is suited for predominantly ionic chemisorption, in which the adsorbate intraorbital relaxation is absent either due to the complete occupation of the adsorbate-induced resonances (limit of anionic chemisorption), or almost complete absence of the electronic charge within the resonances (limit of cationic chemisorption).

Assumption (15) has implications for both the form of the interaction Hamiltonian (2) and the energy spectrum of the initial and final states. In accordance with the WOA, we first introduce the notation

$$\rho(\vec{r}) = \rho_M(\vec{r}) + \rho_m(\vec{r}) \; , \tag{16a}$$

where the subscripts M and m denote the metal and adatom electronic densities, respectively, and expand each of them as

$$\rho_{m,M}(\vec{r}) = \rho^0_{m,M}(\vec{r}) + \delta\rho_{m,M}(\vec{r}) \; , \tag{16b}$$

where $\delta\rho$ measures the fluctuations of the electronic density around the equilibrium distribution ρ^0. Then we substitute (16) into (2) and find that the Hamiltonian of the system can be represented as a sum of unperturbed metal and adatom terms H^0_M and H^0_m, respectively, the terms consisting of the products of ρ^0's, and terms describing the fluctuations of the charge density in the system,

$$H = H^0_m + H^0_M + H^0_{\text{bond}} + H_{\text{rel}} \; , \tag{17a}$$

where

$$H^0_{\text{bond}} = \sum_j \frac{Z_m Z_j}{|\vec{R}_m - \vec{R}_j|} + \int d^3r' \int d^3r'' \frac{\rho^0_M(\vec{r}\,')\rho^0_m(\vec{r}\,'')}{|\vec{r}\,' - \vec{r}\,''|} - \int d^3r' \frac{Z_m \rho^0_M(\vec{r}\,')}{|\vec{R}_m - \vec{r}\,'|} - \sum_j \int d^3r'' \frac{Z_j \rho^0_m(\vec{r}\,'')}{|\vec{R}_j - \vec{r}\,''|} \; ,$$

and

$$H_{\text{rel}} = H^i_{\text{rel}} + H^c_{\text{rel}} \; . \tag{17b}$$

Here,

$$\begin{aligned} H^i_{\text{rel}} = {} & \left[\int d^3r' \int d^3r'' \frac{\rho^0_m(\vec{r}\,'')\delta\rho_M(\vec{r}\,')}{|\vec{r}\,' - \vec{r}\,''|} - \int d^3r' \frac{Z_m \delta\rho_M(\vec{r}\,')}{|\vec{R}_m - \vec{r}\,'|} \right] \\ & + \left[\int d^3r' \int d^3r'' \frac{\rho^0_M(\vec{r}\,')\delta\rho_m(\vec{r}\,'')}{|\vec{r}\,' - \vec{r}\,''|} - \sum_j \int d^3r'' \frac{Z_j \delta\rho_m(\vec{r}\,'')}{|\vec{R}_j - \vec{r}\,''|} \right] , \end{aligned} \tag{17c}$$

and

$$H^c_{\text{rel}} = \int d^3r' \int d^3r'' \frac{\delta\rho_M(\vec{r}\,')\delta\rho_m(\vec{r}\,'')}{|\vec{r}\,' - \vec{r}\,''|} \; . \tag{17d}$$

The static term H^0_{bond} is responsible for the existence of the chemical (covalent) bond in the product state. Now, due to the assumed overall charge neutrality in the system, the two terms appearing in the large parentheses on the rhs of (17c) may be neglected both in the reactant and product states. This, however, would not be the case in ionic chemisorption (cf. Ref. 9). The term H^c_{rel} on the rhs of (17d) describes the relaxation in the system in terms of charge-density fluctuations characteristic of the electronic subsystems, which are coupled by the Coulomb interaction. In the initial state, this term gives rise to the elastic van der Waals attraction between the atom and the metal[24] and its dissipative part can be neglected because of the large energy required to excite real electronic transitions in the atom. On the other hand, broadening of the adatom valence orbitals into resonances in the product state opens a channel for the excitation of localized *low-energy* electronic fluctuations which are coupled to those in the metal, and this term becomes effective in providing a loss mechanism for the inelastic atom-surface reactions. This happens in spite of the assumed overall charge neutrality characterizing the covalent-bond formation (see Sec. III B).

The action of $H^i_{\rm el}$ and $H^f_{\rm el}$ onto the subspaces of initial and final states is now given within the BOA, FCA, and WOA by

$$H^i_{\rm el}\,|\,i,O\,\rangle\,|\,i,o\,\rangle=[V_i(\vec{\rm R}_c)+\epsilon^M_o+\epsilon^m_o)\,|\,i,O\,\rangle\,|\,i,o\,\rangle\;, \tag{18a}$$

$$H^f_{\rm el}\,|\,f,\Lambda\rangle\,|\,f,\lambda\rangle=[V_f(\vec{\rm R}_c)+\epsilon_\Lambda+\epsilon_\lambda]\,|\,f,\Lambda\rangle\,|\,f,\lambda\rangle\;, \tag{18b}$$

where the excitation energies of the charge-density fluctuations in the metal and atom have been denoted by ϵ_Λ (ϵ^M_o) and ϵ_λ (ϵ^m_o) in the excited (ground) state, respectively.

Irrespective of the number of electronic modes excited in the diabatic transition, the transition probability (11) may now be written, with the help of (14), (15), and (18) as

$$P_{\alpha i\to\beta f}=|\,\langle\langle\overline{\beta,f}\,||\alpha,i\,\rangle\rangle\,|^2\int_{-\infty}^{\infty}\frac{dt}{\hbar^2}e^{i(E_{\alpha i}-E_{\beta f}-\epsilon^M_o-\epsilon^m_o)t/\hbar}\langle\, i\,|\,H_{\rm el}(\vec{\rm R}_c)Q_f e^{-iH^f_{\rm el}(\vec{\rm R}_c)t/\hbar}Q_f H_{\rm el}(\vec{\rm R}_c)\,|\,i\,\rangle\;, \tag{19}$$

where we have neglected the effect of the term $H^c_{\rm rel}$ given by (17d) on the initial state $|\,i\,\rangle$ because, due to the discrete energy spectrum in an isolated atom, the charge-density fluctuations can give rise only to interband transitions of energy exceeding the thermal kinetic energies by several orders of magnitude. Hence, within the approximations listed above, the reaction probability assumes a form in which it is given by a product of the Franck-Condon factor characterizing the nuclear diabatic transition and a Fourier transform of a time correlation function which describes the nonadiabatic excitation of the electronic charge-density fluctuations in the product states. These fluctuations give rise to the overall dissipative character of the diabatic transition and hence to the inelasticity of the collision event (reaction).

The expression (19), although formally equivalent to the one given by MG [Eq. (4.11) of Ref. 10], bears a new feature—the allowance for an interplay between the electronic relaxation processes within the metal and the adsorbate. Since this interplay enhances the phase space for relaxation processes, it will also strongly affect the form of the correlation function and the corresponding loss spectrum. In turn, this will have far-reaching consequences for the transition rates and the overall reaction dynamics in covalent chemisorption with respect to the ionic one.

III. CALCULATION OF INELASTIC TRANSITION RATES

A. Correlation function

In the preceding section we brought the expression for the reaction rate P to the form in which the electronic and nuclear dynamics in diabatic transitions are essentially separated. This was possible by making use of a series of approximations described in Secs. II A, II C, and II D. The problem reduces then to the calculation of the Franck-Condon factor and the time correlation function

$$R(t)=\langle\, i\,|\,H_{\rm el}(\vec{\rm R}_c)Q_f e^{-iH^f_{\rm el}(\vec{\rm R}_c)t}Q_f H_{\rm el}(\vec{\rm R}_c)\,|\,i\,\rangle\;. \tag{20}$$

$R(t)$ describes the relaxation of the electronic system when the entire system makes a diabatic transition at the crossing point $\vec{\rm R}=\vec{\rm R}_c$ from the initial, nonbonding state into a final state characterized by the formation of a chemical bond between the adsorbate and the metal. Within the BOA, the transition is induced by the action of $H_{\rm el}$ on the initial diabatic state, since neither the initial nor the final diabatic states are the eigenstates of $H_{\rm el}$. After the transition, the dynamics of electrons is governed by $H^f_{\rm el}$ and the electronic final state may be any excited state of $H^f_{\rm el}$ satisfying the energy conservation expressed through the δ function on the rhs of (11). The dynamics of the electronic relaxation will be determined by $H^c_{\rm el}$ given by (17d). The latter says that the Coulomb interaction between the electrons in the atom and the metal will give rise to charge-density fluctuations within each subsystem. The electronic states involved in this process are those in the metal conduction band around the Fermi energy E_F and in the adsorbate valence resonance, provided the latter is located close to E_F. Customarily, in chemisorption studies, such a relaxation within the adatom is termed as intraorbital, and that within the substrate band states as extraorbital or extra-atomic. The essential prerequisite for intraorbital relaxation is the existence of a non-negligible density of states of the adsorbate-induced valence resonance at E_F, as usually is the case in homopolar or covalent chemisorption.

The concepts of intra- and extra-adsorbate relaxation were first used in connection with the interpretation of the core spectral shapes of adsorbed atoms and molecules.[6,7] In the core spectral problem the event which triggers the relaxation is the sudden appearance of the core hole created in photoemission. In the present problem this role is taken up by the diabatic transition of the system from the initial into the final state [i.e., by the action of the $H_{\rm el}$ on $|\,i\,\rangle$ in (20)] and the consequential change in the electronic interactions from $H^i_{\rm el}$ to $H^f_{\rm el}$ to which the electrons have to adjust themselves. This readjustment is nonadiabatic and may lead to dissipative processes which in turn give rise to inelastic collision and finite reaction rates.

B. Relaxation spectrum

The basic relaxation process emerging from $H^e_{\rm el}$ [Eq. (17d)] and involving coupled excitation of e-h pairs

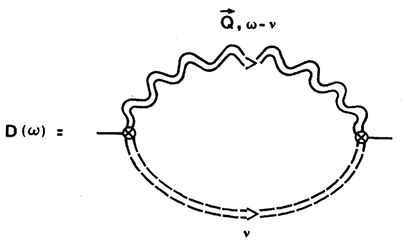

FIG. 2. Basic e-h excitation process in the product state generated by H_{rel}^{c} [Eq. (17d)]. The double wiggly and dashed lines denote the propagation of the charge-density fluctuations described by the spatial Fourier transforms of χ_M and χ_m, respectively [cf. (23) and (24)]. Crossed circles represent vertices pertaining to the Coulomb interaction between the electronic charge-density fluctuations in the atom and the metal.

within the substrate conduction band and the adatom resonance is sketched diagrammatically in Fig. 2. The Coulomb interaction may excite low-energy, charge-density fluctuations within each electronic subsystem, once the diabatic transition has taken place. This means that, in the time representation, the vertices in Fig. 2 are restricted to the same time interval during which H_{el}^{f} is effective.[12,25] As will be shown below, the basic dissipative interaction generated by (17d) and shown in Fig. 2 is inversely proportional to the fourth power of adatom-surface separation. Therefore, it suffices to treat only this leading term in the relaxation processes following the diabatic transition. Let us denote the propagator of the excitations sketched in Fig. 2 by $D(\omega)$. Then

$$S(\omega)=-\frac{1}{\pi}\mathrm{Im}D(\omega) \tag{21}$$

describes the density of excitations taking place in the relaxation event, and ω is the energy such a density-fluctuation mode can absorb from the kinetic energy of the adatom. Since the motion of the adatom nucleus is semiclassical (at least within the BOA and FCA), it behaves as a *localized* perturbation which can either excite or absorb substrate electronic density fluctuations of arbitrary momentum $\vec{\mathrm{Q}}$ parallel to the surface.

To calculate $S(\omega)$, we shall employ linear-response theory. Since we are dealing with low-energy excitations we shall also approximate the atomic and substrate density-density response functions by their linear counterparts. To fix the geometry of the problem, we assume that the intersection of the diabatic curves at which the Franck-Condon transition takes place is located at the point $\vec{\mathrm{R}}_c=(\vec{\mathrm{P}}_c,Z_c)$ outside the surface, where Z is the coordinate perpendicular to the surface, and that the electronic coordinates $\vec{\mathrm{r}}$ are measured either from the adatom center as regards the atomic charge density ($\vec{\mathrm{r}}_m$), or from the coordinate origin at the surface as regards the metal electrons ($\vec{\mathrm{r}}_M$). Thus, the distance between two electrons, one within the adatom and one within the metal, is given by $d=|\vec{\mathrm{R}}_c+\vec{\mathrm{r}}_m-\vec{\mathrm{r}}_M|$. Using this notation and defining the electronic linear-response functions of the metal and the adatom in the coordinate space by $\chi_M(\vec{\mathrm{r}}_m,\vec{\mathrm{r}}'_M,\omega)$ and $\chi_m(\vec{\mathrm{r}}_m,\vec{\mathrm{r}}'_m,\omega)$, respectively, and making use of the two-dimensional Fourier transform of $1/d$, we can write,[24]

$$\begin{aligned}S(\omega)=&-\frac{1}{\pi}\mathrm{Im}\sum_{\vec{\mathrm{Q}},\vec{\mathrm{Q}}'}\left[\frac{2\pi e^2}{Q}\right]\left[\frac{2\pi e^2}{Q'}\right]e^{i(\vec{\mathrm{Q}}-\vec{\mathrm{Q}}')\cdot\vec{\mathrm{P}}_c}e^{-(Q+Q')Z_c}\\&\times i\int_{-\infty}^{\infty}\frac{d\nu}{2\pi}\int d^3r_M\int d^3r'_M e^{-i\vec{\mathrm{q}}\cdot\vec{\mathrm{r}}_M}\chi_M(\vec{\mathrm{r}}_M,\vec{\mathrm{r}}'_M,\omega-\nu)e^{i\vec{\mathrm{q}}'^{*}\cdot\vec{\mathrm{r}}'_M}\\&\times\int d^3r_m\int d^3r'_m e^{i\vec{\mathrm{q}}\cdot\vec{\mathrm{r}}_m}\chi_m(\vec{\mathrm{r}}_m,\vec{\mathrm{r}}'_m,\nu)e^{-i\vec{\mathrm{q}}'^{*}\cdot\vec{\mathrm{r}}_m}\;,\end{aligned} \tag{22}$$

where $\vec{\mathrm{q}}=(\vec{\mathrm{Q}},iQ)$. Exploiting the assumed translational invariance of the surface, we obtain

$$\int d^3r_M\int d^3r'_M e^{-i\vec{\mathrm{q}}\cdot\vec{\mathrm{r}}_M}\chi_M(\vec{\mathrm{r}}_M,\vec{\mathrm{r}}'_M,\omega-\nu)e^{i\vec{\mathrm{q}}'^{*}\vec{\mathrm{r}}_M}=\frac{Q}{2\pi e^2}R_{\vec{\mathrm{Q}}}(\omega-\nu)\delta_{\vec{\mathrm{Q}}\,\vec{\mathrm{Q}}'}\;, \tag{23}$$

where $R_{\vec{\mathrm{Q}}}(\omega)$ is the surface-response function whose properties were calculated earlier.[6,24(b)] The calculation of the second integral proceeds by noticing that only small $\vec{\mathrm{Q}}$ values will contribute significantly to the sum in (22), due to the presence of the quickly converging term $\exp[-(Q+Q')Z_c]$.[24] This enables us to expand the exponentials and obtain

$$\int d^3r_m\int d^3r'_m e^{-i\vec{\mathrm{q}}\cdot\vec{\mathrm{r}}_m}\chi_m(\vec{\mathrm{r}}_m,\vec{\mathrm{r}}'_m,\nu)e^{-i\vec{\mathrm{q}}^{*}\cdot\vec{\mathrm{r}}'_m}=Q^2[\alpha_{\perp}(\nu)+\alpha_{||}(\nu)]\;, \tag{24}$$

where we have introduced the adatom polarizations $\alpha_{\perp}$ and $\alpha_{||}$, perpendicular and parallel to the surface, respectively. Assuming that

$$\alpha_{\perp}(\nu)+\alpha_{||}(\nu)=\alpha_m(\nu)(1+\mu)\;, \tag{25}$$

where $\mu=\alpha_{||}(\nu)/\alpha_{\perp}(\nu)=\text{const}$, we obtain

$$\begin{aligned}S(\omega)=&-\mathrm{Im}\frac{1+\mu}{\pi}e^2\sum_{\vec{\mathrm{Q}}}2\pi Qe^{-2QZ_c}\\&\times i\int_{-\infty}^{\infty}\frac{d\nu}{2\pi}\alpha_m(\nu)R_{\vec{\mathrm{Q}}}(\omega-\nu)\;.\end{aligned} \tag{26}$$

As expected, (26) states that $S(\omega)$ is proportional to the imaginary part of the convolution of the response functions characterizing each electronic subsystem.

To evaluate the sum and the integral in (26) we shall adopt the model expressions for the response functions $\alpha_m(\nu)$ and $R_{\vec{Q}}(\nu)$, as calculated in Refs. 6 and 7(a). Their form can be evaluated via Kramers-Kronig relations once their respective spectral densities $(\hbar/2m\nu)S_m(\nu)=-\mathrm{Im}\,\alpha_m(\nu)/\pi$ and $S^{e\text{-}h}_{\vec{Q}}(\nu)=-\mathrm{Im}\,R_{\vec{Q}}(\nu)/\pi$ are known. Thus, we have

$$S_m(\nu)=\nu\tilde{\rho}^{\,2}_m(0)+\frac{\nu^3}{3!}\{2\tilde{\rho}^{\,\prime\prime}_m(0)\tilde{\rho}_m(0)-[\tilde{\rho}^{\,\prime}_m(0)]^2\}+O(\nu^5) \tag{27a}$$

and

$$S^{e\text{-}h}_{\vec{Q}}(\nu)=\frac{2\nu Q}{\pi\sqrt{3}\,\omega_p k_{\mathrm{TF}}}\left[\ln\frac{2k_{\mathrm{TF}}}{Q}-\frac{1}{2}\right]-\frac{2}{3\pi}\left[\frac{\nu}{\omega_p}\right]^2+O(\nu^3)\,, \tag{27b}$$

where ν is the excitation energy of an e-h pair and $\tilde{\rho}_m(0)$, ω_p, k_{TF}, and v_F denote the adsorbate-resonance-level density of states at E_F, substrate plasmon frequency, Thomas-Fermi wave vector, and Fermi velocity, respectively. Next, we will simplify these expressions by introducing an exponential cutoff instead of a power series in ν. The cutoff must be determined from the requirement that the maxima of (27) be invariant to the functional form of a cutoff. In this way, we obtain the *Ansätze*[6,7(a)]

$$S_m(\nu)=\nu\tilde{\rho}^{\,2}_m(0)e^{-\nu\tilde{\rho}_0(0)} \tag{28a}$$

and

$$S^{e\text{-}h}_{\vec{Q}}(\nu)=-\frac{1}{\pi}\mathrm{Im}\,R_{\vec{Q}}(\nu)=\frac{2\nu Q}{\pi\sqrt{3}\,\omega_p k_{\mathrm{TF}}}\left[\ln\frac{2k_{\mathrm{TF}}}{Q}-\frac{1}{2}\right]e^{-\nu/Qv_F}\,. \tag{28b}$$

Substituting these expressions into (26), carrying out the frequency integration, and recalling that

$$\sum_{\vec{Q}}\to\frac{L^2}{(2\pi)^2}\int d^2Q\,,$$

where L^2 is the unit area of the surface, we obtain, after a tedious calculation,

$$S(\omega)\simeq\frac{\hbar(1+\mu)e^2\tilde{\rho}^{\,2}_m(0)}{2m\sqrt{3}\,\pi\omega_p k_{\mathrm{TF}}}\frac{\ln(2k_{\mathrm{TF}}Z_c/1.65)}{(2Z_c)^4}\times\omega^2\exp\left[-\omega\left[\frac{Z_c}{v_F}+\tilde{\rho}_m(0)\right]/2\right]. \tag{29}$$

It is seen that the excitation spectrum (28) is softer ($\sim\omega^2$) than any of the constituents of the convolution (26), i.e., $S_m(\omega)$ and $S^{e\text{-}h}_{\vec{Q}}(\omega)$, which are linear in ω for $\omega\to 0$. This is so because the existence of two types of the excitation modes (within the adatom resonance and the metal) enhances the phase space of relaxation through low-energy e-h pairs. This effect is reminiscent of the effect of recoil in the studies of interactions of mobile particles with low-energy excitations in a Fermi gas.[26,5,27] The softness of the spectrum (29) will have strong physical implications on the correlation function (20) and thereby on the transition rates (19) as well.

C. Calculation of the loss spectrum

Knowledge of the relaxation spectrum (29) enables us to calculate the temporal properties of the correlation function (20). Upon observing that the evolution of the electronic system, after the diabatic transition, is governed strictly by H^f_{el}, we may reduce the problem to the application of the famous method of Nozières and de Dominicis[12] outlined in their study of x-ray-emission and -absorption edges in metals. Applying this method to the present case, we obtain[25,6,27]

$$R(t)=|V_{if}(\vec{\mathrm{R}}_c)|^2\times\exp\left[-\int_0^\infty d\omega'\frac{1-e^{-i\omega' t}-i\omega' t}{\omega'^2}S(\omega')\right], \tag{30}$$

where

$$V_{if}=\langle i\,|H_{\mathrm{el}}(\vec{\mathrm{R}}_c)|\,f\rangle \tag{31}$$

is the perturbation matrix element responsible for the diabatic transition. The Fourier transform of (30) gives the loss spectrum appearing in the expression (19) for the transition rate $P_{\alpha i\to\beta f}$. Introducing the abbreviations

$$a=\frac{\hbar(1+\mu)e^2\tilde{\rho}^{\,2}_m(E_F)}{2m\sqrt{3}\,\pi_p k_{\mathrm{TF}}}\frac{\ln(2k_{\mathrm{TF}}Z_c/1.65)}{(2Z_c)^4} \tag{32a}$$

and

$$b=\frac{1}{2}\left[\frac{Z_c}{v_F}+\tilde{\rho}_m(E_F)\right], \tag{32b}$$

which help us to simplify the notation in (29), we may perform the time integral in (19). The details of this calculation are given in the Appendix. Eventually, we find that the transition rate may be cast in the form

$$P_{\alpha i\to\beta f}(\omega)=\frac{2\pi}{\hbar}|\langle\!\langle\overline{\beta,f}||\alpha,i\rangle\!\rangle|^2|V_{if}(\vec{\mathrm{R}}_c)|^2e^{-(a/b)}\times\left[\delta(\omega)+ae^{-b\omega}\sum_{n=1}^{\infty}\frac{(a\omega)^{n-1}}{n!(n-1)!}\right]\Theta(\omega)\,, \tag{33a}$$

where

$$\omega=E_{\alpha i}-E_{\beta f}+\epsilon^M_o+\epsilon^m_o-\epsilon_\Lambda-\epsilon_\lambda+a/b^2 \tag{33b}$$

is the energy dissipated to the e-h pairs in the inelastic diabatic transition. A plot of

$$\tilde{P}(\omega)=P(\omega)/[(2\pi/\hbar)|\langle\!\langle\beta,f||\alpha,i\rangle\!\rangle|^2|V_{if}(\vec{\mathrm{R}}_c)|^2]$$

as function of ω for a reasonable choice of parameters a and b (cf. Sec. IV) is shown in Fig. 3. Since a measures

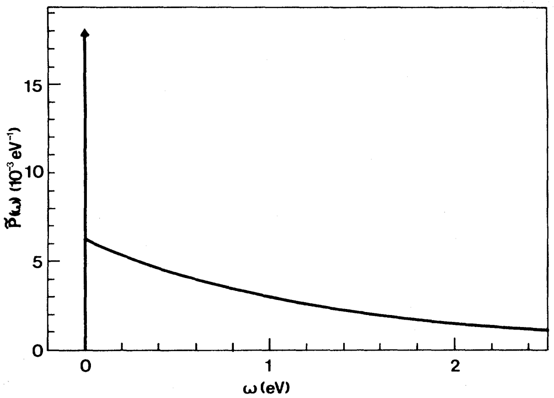

FIG. 3. Energy-loss spectrum $\tilde{P}(\omega)$ entering the expression for the transition rate (33a), for $a=0.62\times10^{-2}$ eV^{-1} and $b=0.73$ eV^{-1} (cf. Sec. IV). δ-function no-loss peak is denoted by the arrow at the origin. Weight of the no-loss peak ≈0.99, mean-energy transfer $\omega_1=12$ meV.

the coupling between the charge-density fluctuations in the two subsystems, the value of (33a) for $a\to0$ describes the pure "predissociation" behavior of atom-surface collisions, viz.,

$$P^0_{\alpha i\to\beta f}(\omega)=(2\pi/\hbar)\,|\langle\langle\beta,f\,||\,\alpha,i\rangle\rangle|^2\,|V_{if}(\vec{R}_c)|^2\delta(\omega)\ . \tag{34}$$

This expression is analogous to the one obtained by Landau[16] and Zener[17] in their studies of energy-level crossing and predissociation in diatomic molecules. This leads us to identify the remainder of the expression (33a) with the loss spectrum $\tilde{P}(\omega)$ which determines the inelasticity of the transition rate. The exponential factor in front of the opening large parenthesis in (33a) gives the intensity of the elastic line (i.e., of the δ function) and plays the role of an electronic Debye-Waller factor, which weighs the overall elastic scattering probability into the channel (β,f).

D. Perturbation matrix element

The calculation of the perturbation matrix element $V_{if}(\vec{R}_c)$ in (33a) is very difficult, since it requires knowledge of the electronic wave functions of the reactant and product states. Similar types of matrix elements appear commonly in quantum chemistry in the studies of molecular spectra.[28] However, since the diabatic electronic wave functions corresponding to various adsorption problems are presently unknown, we may try to estimate the magnitude of V_{if} by using some simplifying assumptions and by resorting to some intuitively valid approximations.

Let us assume that the adatom-substrate bond formed in the diabatic transition is localized mainly between the adatom and the nearest surface atom in the metal. In this "surface-molecule" approximation, we expect that the bond would be very close to the one formed in a corresponding diatomic molecule if such may exist. First-principles calculations for diatomics[29] and chemisorption on surfaces[30] indeed confirm this assumption for the ground-state electronic configurations and at equilibrium distances. Assuming the problem is similar to the one encountered in the studies of diatomics, we may then resort to the types of approximations used there in order to estimate the magnitude of V_{if}.

In the predissociation studies of alkali halides, in which the initial electronic configuration is characterized by a homopolar state and the final one is characterized by almost complete ionization of the constituents, V_{if} was estimated as[20]

$$V_{if}^{\text{ion}}(\vec{R})\simeq\int m(\vec{r}_1)x(\vec{r}_2)H_{\text{el}}(\vec{R})x(\vec{r}_1)x(\vec{r}_2)d^3r_1d^3r_2 \approx\frac{S_{mx}(R)}{cR}\ , \tag{35}$$

where $m(\vec{r}_1)$ and $x(\vec{r}_2)$ denote the initial states of the electron 1 in the outer s orbital on an alkali nucleus and the electron 2 in the outer $p\sigma$ orbital in a halogen, respectively, and $S_{mx}(R)$ is the overlap between the two orbitals. The value of the constant c used in calculations varied between 2 and 8.

The same procedure could not be used to estimate V_{if} in the case of covalent-bond formation, because the final electronic states are not localized within the single ion, but rather shared between the two atoms. Hence, in the present situation, the molecular-orbital approach lends itself as a method suitable for giving a qualitative estimate of the behavior of $V_{if}(\vec{R})$. We may write the wave function of an electron participating in the final-state covalent bond as an appropriate linear combination of the atomic orbitals $|m'\rangle$ and $|x'\rangle$ of the constituent atoms,[28]

$$\phi_f(\vec{r})=\frac{1}{N}\left[\sum_{m'}A_{m'}m_{m'}(\vec{r})+\sum_{x'}C_{x'}x_{x'}(\vec{r})\right]\ , \tag{36}$$

where N, $A_{m'}$, and $C_{x'}$ are the normalization constant and the appropriate coefficients, respectively. Neglecting spin, we obtain

$$V_{if}(\vec{R})=\int m(\vec{r}_1)x(\vec{r}_2)H_{\text{el}}(\vec{R})\phi_f(\vec{r}_1)\phi_f(\vec{r}_2)d\vec{r}_1d\vec{r}_2\ . \tag{37}$$

Now we may employ the arguments of Ref. 20 which led to the expression (35), to further approximate (37) to the form

$$V_{if}(\vec{R})\approx\frac{1}{cRN^2}B[S_{mx}(\vec{R})]\ , \tag{38}$$

where B denotes the appropriate bilinear function of various overlaps $S_{mx}(R)$ emerging from the expansion (36). Thus, for instance, in the simple case of a single atomic orbital per atom and with $A_{m'}=\delta_{mm'}$, $C_{x'}=\pm\delta_{xx'}$ (symmetric molecule), one would obtain

$$\frac{B(S_{mx})}{N^2}=\frac{1\pm2S_{mx}+S_{mx}^2}{2(1\pm S_{mx}^2)}$$

for the ground (+) and the first excited state (−) of the surface molecule, respectively. The value of $V_{if}(\vec{R})$ at $\vec{R}=\vec{R}_c$ would then represent the order of magnitude estimate of the diabatic transition potential matrix element appearing in the expression for the reaction rate (33a).

E. Franck-Condon nuclear overlap integral

The basic quantum-mechanical features of the nuclear transition from one to the other diabatic curve are contained in the Franck-Condon overlap integral introduced in Sec. II C. Its calculation may be reduced to the evaluation of the nuclear overlap

$$S_N=\int dZ\,\chi_v(Z)\chi(Z)\ , \qquad (39)$$

where χ_v is the wave function of a vibrational nuclear state, in the potential $V_f(R)$, generally of a finite lifetime due to predissociation, and χ is a continuum wave function. An integral of the form (39), for the collision of the second kind $[E>V_f(\infty)>V_i(\infty)]$, was calculated by Landau[16] under the assumption that the classical turning points were far outside the region of curve crossing. Application of the WKB method then yielded the famous Landau-Zener formula.

In the present case, in which $V_f(\infty)>E>V_i(\infty)$, the turning point of the continuum wave function $\chi(Z)$ is likely to appear near the curve-crossing point, a situation studied by O'Malley.[21] In the vicinity of the turning point Z_E, χ will be well represented by an Airy function with a sharp maximum at Z_E provided the slope V' of $V_i(Z_E)$ is considerably different from zero. Assuming this, one can obtain an expansion of $\chi(Z)$ in inverse powers of a large quantity,

$$\lambda=2V_i'(Z_E)Z_{\min}/\hbar\Omega_0\ , \qquad (40)$$

where $Z_{\min}$ and $\hbar\Omega_0$ are the zero-point amplitude of the oscillator χ_v and its quantum of energy, respectively, by making use of the integral representation of the Airy functions. Thus, one obtains[21]

$$\chi(Z)\simeq(\alpha^2/V')^{1/2}[1-(1/3\lambda)d^3/dx_E^3]\delta(x-x_E)\ , \qquad (41)$$

where $x=\alpha Z$ and $\alpha=Z_{\min}^{-1}$. Such an $\chi(E)$ is normalized to the δ function of energy. This leads to the following expression for the overlap:

$$S_N=[V'(Z_E)]^{-1/2}\tilde{\chi}_v(Z_E)\ , \qquad (42)$$

where

$$\tilde{\chi}_v(Z)=\chi_v(Z)-\frac{1}{3\lambda}\chi_v'''(Z)\ ,$$

χ_v is considered known. The dimension of S_N is determined by the normalization of $\chi(E)$ and χ_v.

Expression (42) is the desired order-of-magnitude estimate of the nuclear overlap and shows that one of the maxima (minima) of χ_v must coincide with the maximum of χ at the turning point in order to produce a nonnegligible overlap and, consequently, the nonvanishing probability amplitude for the Franck-Condon transition.

The differential cross section or the probability of the reaction is obtained by dividing the transition rate $P(\omega)$ by the perpendicular-to-the-surface component of the current $J_Z(E)$ of the reactant.[31] As J_Z depends on the normalization of $\chi(E)$, which, in the present case, is normalized to the δ function of energy, we obtain $J_Z(E)=(2\pi\hbar)^{-1}$ and

$$\frac{d\sigma_{\text{react}}}{d\omega}=2\pi\hbar P_E(\omega)\ , \qquad (43)$$

where E is the initial kinetic energy of the reactant.

IV. DISCUSSION

The basic result of this work is contained in expression (33a), which gives the probability $P_{\alpha i\to\beta f}$ that an atom (molecule) will make a diabatic transition from the initial state characterized by the quantum numbers α and i, denoting the nuclear motion and the electronic configuration, respectively, into the product state characterized by a covalent-bond formation and the corresponding quantum numbers β and f (cf. Sec. II A). The transition may be either elastic or inelastic. In the former case the system will exhibit a predissociation behavior in the product state and the probability of such an event is weighted by an electronic Debye-Waller factor $\exp(-a/b)$, which multiplies the no-loss line in (33a). In the case of inelastic transitions, a portion of the atomic nuclear kinetic energy ω is dissipated to the electronic degrees of freedom whose excitation spectrum is described by the second term in large parentheses on the rhs of (33a). The quantitative features of this loss spectrum are determined by the various parameters of the system contained in the constants a and b given by (32). In particular, if the resonance density of states $\tilde{\rho}_m(E_F)$ at the Fermi level were zero, there would be no relaxation within the system [because of our neglect of the terms in large parentheses in (17c) which appear in the case of ionic bonding], and one would observe only the elastic transitions.

A quantity which measures the efficiency of dissipation of the atomic nuclear kinetic energy in the adiabatic transition described is the average energy loss or the first moment ω_1 of the loss spectrum in (33a). A straightforward calculation gives

$$\omega_1(a,b)=a/b^2\ . \qquad (44)$$

This quantity should now be compared with the average thermal energies of nuclear motion of reactants prior to a diabatic transition and with the separation between two vibronic levels of the final-state potential $V_f(Z)$. To obtain an estimate of ω_1 for a realistic system, we may consider a copper substrate because its conduction-band density of states at the Fermi level is free-electron-like. In this case, the low-energy electronic response of the surface should be adequately represented by the surface-response function $R_{\vec{Q}}(\nu)$, whose spectrum $S_{\vec{Q}}^{e\text{-}h}(\nu)$ (Refs. 6 and 32) is given by (28b). Next, we shall assume that, at the diabatic curve crossing Z_c, the adsorbate induced density of states $\tilde{\rho}_m(E)$ is approximately given by a Lorentzian whose full width at half-height is $2\Delta=0.5$ eV, which is a smaller value than at the equilibrium distance Z_0 (cf. Fig. 3 in Ref. 30). With free-electron parameters $k_{\text{TF}}=0.3a_B^{-1}$ and $v_F=2.95\times10^{16}a_B\ \text{s}^{-1}$ (a_B denotes Bohr radius) for copper known,[33] we may obtain a and b as functions of Z_c. Knowledge of Z_c is of crucial importance because $a\propto Z_c^{-4}$. In general, it may be expected that, for covalent bonding, the intermolecular distances at diabatic curve crossings would be considerably smaller than in the case of ionic bonds, where the "harpooning mechanism" is known to be effective.[34] Thus, for instance, the switch of the covalent bond in $H + H_2 \rightarrow H_2 + H$ reaction is known to occur at a distance smaller than $4a_B$.[35] If we take this value as representative of covalent bonding, we obtain lower bound estimates $a = 0.62\times10^{-2}$ eV^{-1} and $b = 0.73$ eV^{-1}. Hence,

$$\omega_1(Z_c = 4a_B) = 12 \text{ meV} , \tag{45}$$

which would be quite a substantial energy loss for a thermalized particle. At $Z_c = 3a_B$ the value of ω_1 rises to 26 meV and at $Z_c = 5a_B$ it drops to 2 meV, assuming the same Δ. On the other hand, the first moment of the loss spectrum discussed by GM,[9] and pertinent to ionic chemisorption, can be estimated[36] to be $\omega_1^{\mathrm{GM}} = 70$ meV for $Z_c = 4a_B$ and the same free-electron parameters of the substrate (also see below). Of course, one could anticipate even larger energy losses in the case where the charge-density fluctuations in the substrate valence bands, located at the Fermi level, would also participate in the relaxation processes. Such a situation may be expected for a majority of transition-metal substrates.

We may now make a comparison with the results of Gadzuk and Metiu,[9] who studied ionic chemisorption reaction rates. Since their treatment and this one consider two different relaxation terms in the electronic part of the Hamiltonian [cf. discussion following (17)], it is clear that the two theories supplement each other in covering the possible electronic relaxation processes induced by diabatic transitions. However, due to the different types of chemical bonds formed in the product states, the resulting loss spectra exhibit very different behavior. The charge transfer in the ionic bond formation gives rise to a loss spectrum whose weight is concentrated around the threshold, where, in fact it exhibits an infrared singularity, and a zero-weight no-loss line. [The first moment ω_1^{GM} of this spectrum is proportional to Z_c^{-3} (Ref. 6); however, the slower falloff of ω_1^{GM} with distance may, to some extent, be compensated for by larger Z_c, which is characteristic of the homopolar-ionic diabatic crossing[9,34].] These features originate from the sudden ionization of the adatom in the diabatic transition and a single-channel relaxation through substrate conduction electrons only. On the other hand, in the case of covalent bonding studied in the present paper, an additional channel of relaxation via the adatom valence resonance excitations becomes effective after the diabatic transition, and this leads to the enhancement of the phase space for relaxation. This enhancement of the phase space quenches the Anderson orthogonality (i.e., the infrared singularity) and, in a sense, takes over the role which would be played by recoil in the x-ray-edge problem[26,5] and surface scattering.[27] For this reason, the spectrum (33a), characteristic of the covalent product state, exhibits the elastic or the no-loss line weighted by an electronic Debye-Waller factor $\exp(-a/b)$. The loss spectrum has a shape of a sideband (cf. Fig. 3), in contrast to the singular threshold behavior found in the case of an ionic product state. These differences can also be thought of as being due to the different charge redistribution in the nonadiabatic screening processes pertinent to a nonadiabatic formation of ionic and covalent chemisorption bonds.

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APPENDIX

We wish to evaluate the integral

$$\widetilde{P}(\omega) = -\frac{1}{\pi}\,\mathrm{Im}\int_{-\infty}^{\infty} dt\, e^{i\omega t} e^{C(t)}\Theta(t) , \tag{A1}$$

where $C(t)$ is given by the exponent appearing in (30),

$$C(t) = -\int_0^{\infty} d\omega' \frac{1-e^{-i\omega' t}-i\omega' t}{\omega'^2} S(\omega') , \tag{A2}$$

and $S(\omega')$ is given by (29),

$$A(\omega') = a\omega'^2 e^{-b\omega'} , \tag{A3}$$

where a and b have been defined by Eq. (32). Substituting (A3) into (A2) and evaluating the integrals, we obtain

$$C(t) = i\frac{a}{b^2}t - \left(\frac{a}{b}\right)\left[1-\left(1+\frac{it}{b}\right)^{-1}\right] . \tag{A4}$$

The first term on the rhs of (A4) may be associated with $\exp(i\omega t)$ in (A1), as it only shifts the threshold energy. Thus, we are left with the integral of the form

$$P(\omega) = -\frac{1}{\pi}\,\mathrm{Im}\int_0^{\infty} dt\, e^{i\omega t}\exp\left\{-\left(\frac{a}{b}\right)\left[1+\left(\frac{ib}{t-ib}\right)\right]\right\} = \frac{1}{2\pi}e^{-(a/b)}\int_{-\infty}^{\infty} dt\, e^{i\omega t}\exp\left[-\left(\frac{ib}{t-ib}\right)\right] . \tag{A5}$$

Expanding the second exponential in the integrand of (A5), we find that the resulting series can be integrated term by term by using tabulated integrals.[37] Hence,

$$\widetilde{P}(\omega) = e^{-(a/b)}\left(\delta(\omega) + a\, e^{-b\omega}\sum_{n=1}^{\infty}\frac{(a\omega)^{n-1}}{n!(n-1)!}\right)\Theta(\omega) , \tag{A6}$$

which is the desired spectrum normalized to unity.

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