Desorption Induced by Multiple Electronic Transitions

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A new mechanism is introduced to describe desorption from surfaces under conditions of strong electronic excitation. When repetitive excitations occur within the relaxation time for the adsorbate-surface vibration, the process of desorption induced by multiple electronic transitions may provide an enhancement of orders of magnitude over a single-excitation mechanism. This generalization of the classic Menzel-Gomer-Redhead picture encompasses within one formalism both single-excitation processes and a thermal limit. The mechanism may be operative in desorption by femtosecond laser pulses.

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Desorption induced by electronic transitions (DIET) [1] is a subject of great fundamental [2] and practical significance [3] in surface science. A general framework for DIET processes was introduced in 1964 by Menzel, Gomer, and Redhead [4]. The initial step in this process is a Franck-Condon transition from the ground potential energy surface (PES) V_g of the adsorbate complex to an excited state V_e. While moving on the excited PES, the adsorbate converts potential energy into kinetic energy. In a semiclassical picture, desorption results whenever the adsorbate remains in the excited state for the critical time τ_c needed to attain positive total energy upon return to the ground state. Trajectories for adsorbates experiencing motion on the excited PES for times less than and greater than τ_c are illustrated in Figs. 1(a) and 1(b), respectively. Both trajectories start with a vertical transition from V_g to V_e. In 1(a), the adsorbate is accelerated toward the surface after excitation [5], but is deactivated before τ_c. The energy gained results in vibrational excitation in the ground state, but is insufficient for desorption. In 1(b), the adsorbate remains on V_e for a time greater than τ_c. It then escapes from the ground-state well after deactivation. The efficiency of this process depends critically on the excited-state lifetime τ. The probability of desorption P can be estimated by the likelihood of the adsorbate remaining on the excited PES for a time $t > \tau_c$, i.e., as $P \sim \exp(-\tau_c/\tau)$. Since adsorbate lifetimes on excited PES are typically quite short, low DIET yields are often observed.

In this Letter, we discuss a generalization of the usual DIET picture to include desorption induced by *multiple* electronic transitions (DIMET). As in DIET, the initial step is a Franck-Condon transition to the excited PES [Fig. 1(c)]. If the adsorbate remains on the excited PES for a time $t < \tau_c$, then it cannot escape from the well upon returning to the ground state V_g. While in the conventional DIET scheme this particle will not contribute to the desorption yield, in DIMET it may be reexcited and desorb. Figure 1(c) shows such a case. The adsorbate makes another Franck-Condon transition, but this time from a vibrationally excited level of the ground PES. The additional energy associated with the vibrational excitation allows the adsorbate to desorb more readily than after the first excitation. On the other hand, in the limit where excitations are separated by more than the lifetime of the adsorbate-surface vibration, the DIMET mechanism simply reverts to n iterations of a conventional DIET process.

Conditions appropriate for a DIMET mechanism are obtained in recent experiments in which desorption from adsorbate-covered metal surfaces is induced by femtosecond laser pulses [6–9]. These studies indicate that the high density of electronic excitations produced by the

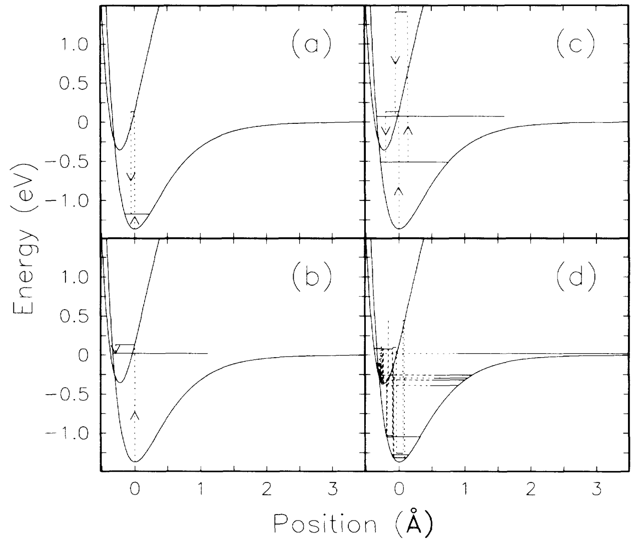

FIG. 1. Trajectories for motion on the ground and excited PES. The dotted lines represent the total energy of the adsorbate complex, with vertical segments arising from Franck-Condon transitions and horizontal segments from conservative motion on a given PES. (a),(b) Trajectories displayed associated with a single-excitation DIET process. (a) and (b) correspond, respectively, to cases where the particle remains in the excited PES for less than or greater than τ_c, the critical time for desorption. (c),(d) Trajectories for the DIMET process. (c) is a simplified example of DIMET with two excitation-deexcitation cycles, while (d) is the result of a complete simulation with $\tau = 2$ fs and peak electronic temperature of $T_e = 5500$ K.

ultrafast laser pulse is crucial for desorption. Here we examine the DIMET mechanism in the context of femtosecond desorption experiments on NO/Pd(111) [6-8]. Since our primary goal in this work is to develop a general understanding of DIMET and how this process compares with the single-excitation limit, we have adopted the type of simplified model already introduced to describe DIET in related systems. Rigid one-dimensional PES are assumed and the molecular dynamics on them is treated in a semiclassical fashion with Franck-Condon transitions occurring stochastically [10]. In DIET studies, the effect of the damping of the adsorbate-surface vibration is generally neglected, and we have made the same approximation in this work. In a complementary study, we have investigated the role of nonadiabatic coupling on a *single* PES surface [11]. A complete model taking into account both nonadiabatic coupling on a given PES and the role of interpotential excitations is currently being developed.

The ground PES in our model is taken to be of the Morse form with a well depth of 1.4 eV chosen to reproduce the measured desorption rate for NO/Pd(111) at 500 K and a range parameter determined by the molecule-surface vibrational frequency of $\hbar\omega = 41$ meV [12]. For the excited PES, we adopt the expression for a negative ion applied by Gadzuk *et al.* [13] to describe DIET processes in the NO/Pt(111) system [14]. This potential is constructed from the ground-state potential by adding a constant given by the energy required to transfer an electron from the metal to the isolated NO molecule (5 eV) and a spatially dependent term representing the interaction of the ion with its image charge. In our calculation the effective image plane is located 1.0 Å from the molecule toward the surface.

To complete the model we must specify rates for transitions between the two PES. We write the deactivation rate as a product of a position-dependent hopping rate [15] from the negative ion into the metal and a statistical factor to account for availability of the electron final state at electronic temperature T_e,

$$k_d(z) = [\tau^{-1} e^{-z/z_d}][1 - f(\varepsilon_A(z), T_e)] \,. \tag{1}$$

The lifetime of the excited state at the well minimum is denoted by τ and calculations are presented below for 1 fs $< \tau <$ 5 fs. The range parameter is maintained at $z_d = 0.3$ Å, a value comparable to the exponential decay of the repulsive part of the potential energy surfaces. The energy in the Fermi factor, $\varepsilon_A(z)$, is the energy to promote an electron from the chemical potential to the NO affinity level, defined in terms of the PES separation, $\varepsilon_A(z) = V_e(z) - V_g(z)$. Similarly, we write the activation rate as

$$\begin{aligned} k_a(z) &= [\tau^{-1} e^{-z/z_d}] f(\varepsilon_A(z), T_e) \\ &= k_d(z) \exp\{-\varepsilon_A(z)/k_B T_e(t)\} \,. \end{aligned} \tag{2}$$

The electronic temperature profiles $T_e(t)$ were obtained using a coupled diffusion equation formalism described previously [6-8]. For a Pd surface irradiated by a 200-fs laser pulse, $T_e(t)$ rises in a time slightly longer than the laser pulse and decays roughly exponentially in ~ 1 ps [8]. For an absorbed fluence of 6.5 mJ/cm^2 used below, a peak electronic temperature of 5500 K is reached, with a lattice temperature rise of less than 500 K.

A representative desorbing trajectory is shown in Fig. 1(d) for $\tau = 2$ fs. In this example, the particle experiences 20 cycles of excitation and deexcitation before escaping from the well. From a calculation of 6.4×10^4 trajectories [16], we find an average of 21 excitations for the desorbing particles but a mean of only 12 for all particles. Clearly desorption is favored by a high number of excitation cycles. Because of the frequency excitations, the average energy gain per excitation for DIMET is less than 69 meV, and the average lifetime on the excited PES during each excitation is just 3.1 fs. Thus no segment in the DIMET trajectory must involve an improbable event. On the other hand, for the conventional DIET process the particle must follow a highly atypical trajectory, staying on the excited PES for 25 fs in order to gain the required 1.4 eV in one step. Note, however, that the *aggregate* time spent on the excited PES in the DIMET process is 66 fs, considerably greater than for DIET. This result reflects the fact that energy may be lost as well as gained during an excitation cycle in DIMET depending on the relation between the adsorbate velocity and the slope of the excited PES.

The desorption probability for the DIMET process with $\tau = 2$ fs is $P_{\text{DIMET}} = 9 \times 10^{-4}$. For comparison, the single-excitation DIET probability is $P_1 = 4.5 \times 10^{-9}$. To calculate the overall desorption probability for an incident laser pulse by a traditional DIET process, we must multiply P_1 by the average number of excitations n_{ex} per adsorbate. For either direct photoinduced processes in the adsorbate complex [17] or a substrate-mediated mechanism [14,18], we may construct an upper bound for n_{ex} by assuming that all of the incident energy is consumed in transitions to the excited PES of the adsorbate. This condition implies $n_{\text{ex}} < 63$ and $P_{\text{DIET}} = n_{\text{ex}} P_1 < 2.8 \times 10^{-7}$. Thus, the DIMET process provides an enhancement of the desorption rate by more than a factor of 10^3 compared with a conventional DIET mechanism for the present conditions.

The highly nonlinear rise in DIMET efficiency with laser fluence is shown in Fig. 2 along with the contrasting linear DIET desorption probability. Figure 3 shows the dependence of the DIET and DIMET processes on the excited-state lifetime τ. With increasing deactivation rate, P_1 drops precipitously. For the DIMET process, an increasing deactivation rate is also seen to give a lower desorption probability. The effect, however, is much weaker and P_{DIMET}/P_1 exceeds 10^8 for small values of τ. For DIMET, the desorption yield decreases with increasing deactivation rate because each excursion to the excited potential is briefer and produces a smaller change in

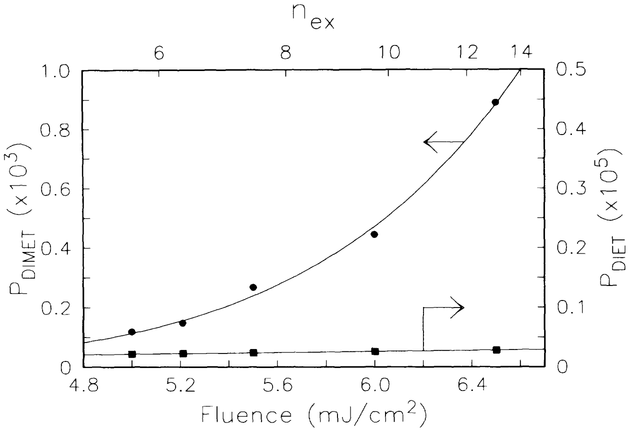

FIG. 2. Desorption probability for DIMET and an upper bound for a DIET as a function of laser fluence from stochastic trajectory simulations (shown together with power-law fits). The corresponding average number of excitations for all adsorbates in the DIMET calculation is indicated in the upper scale. The range of fluences corresponds to peak T_e between 4600 and 5500 K. The excited-state lifetime is $\tau = 2$ fs.

the energy of the adsorbate, but the effect is mitigated by the increased number of excitations implied by Eq. (2).

In comparing the simulations of the DIMET process with the experimental results for femtosecond desorption, we find that a number of the key properties can be reproduced at a qualitative level. First, the highly nonlinear dependence of the desorption yield on laser fluence arises naturally in a DIMET process. Second, in accord with experiment, the predicted desorption yield is far greater than that anticipated for a simple DIET process. The DIMET model also predicts relatively low kinetic energies of the desorbed particles and a narrow temporal correlation feature [7,8], as observed experimentally. Quantitatively, however, the calculated desorption yield, although very parameter sensitive (as in Fig. 3), is generally lower than in the experiment. Lack of quantitative agreement is to be expected given the simplified nature of the model. A complete treatment would require features such as more realistic PES [19], treatment of the internal degrees of freedom of the NO molecule [20], and inclusion of substrate coupling to the adsorbate-surface vibration [21,22] on each PES. The influence of the latter may be of particular importance in light of recent measurements of adsorbate vibrational relaxation on the picosecond time scale [23]. Coupling of the adsorbate vibration to the substrate electronic excitation [11] might be expected to enhance the desorption yield, while coupling to the substrate phonons should have the opposite effect.

Finally, we remark that in the present model the molecule-surface vibrational excitation approaches a thermal distribution at temperature T_e. However, because of the small energy transfer during each excitation-deexcitation cycle in the DIMET process, full equilibration can be achieved only after many cycles. The simulations above correspond to a transient regime in which there are enough cycles to give an approximately thermal distribution for the molecule-surface vibration, but the number is insufficient for full equilibration leading to a vibrational temperature below T_e. This behavior is analogous to that obtained using a Langevin equation for the adsorbate motion on a single PES in the presence of a frictional coupling to the electronic excitation [11]. In this regime, the desorption rate can be described by an Arrhenius expression with an activation energy given by the well depth. For less rapidly varying electronic temperatures (on a time scale of a few picoseconds for the current temperature range), full equilibrium of the molecule-surface vibration with T_e is obtained. Thus, DIMET can bridge the gap between the highly nonequilibrium behavior associated with DIET and a process occurring in the usual manner for thermal desorption. One should note, however, that the DIMET mechanism is not restricted to situations in which an equilibrium electronic energy distribution in the substrate is assumed. Further discussion and delineation of these different regimes of the DIMET process will be presented elsewhere.

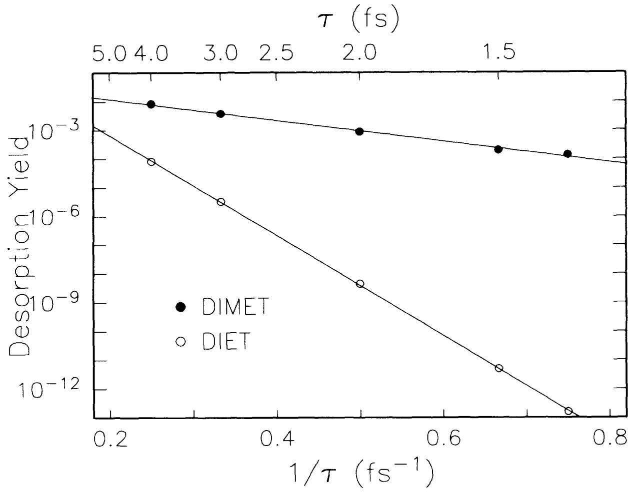

FIG. 3. Desorption probability by DIMET (P_{DIMET}) and by single-excitation DIET (P_1) as a function of excited-state lifetime τ obtained from trajectory calculations with a peak electronic temperature of 5500 K.

In conclusion, we have introduced a new mechanism for desorption arising when repetitive electronic transitions occur within the vibrational relaxation time of an adsorbate. The mechanism provides a strong enhancement to the desorption yield compared with a traditional DIET process and exhibits a nonlinear dependence on the excitation rate, features needed to explain experimental data on desorption induced by femtosecond laser pulses. The mechanism reduces, in different regimes, to a single-excitation DIET process and to an electronically driven thermal process. DIMET may be relevant in other physical situations in which electronic excitation is present. For example, high densities of electronic excitation are known to accompany desorption arising from bombardment of surfaces by very energetic particles [24]. Further, the general concept of a strong enhancement to rates from repetitive electronic excitation may be significant in a variety of physical processes beyond that of desorption from surfaces.

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