# Photoinduced Desorption of Molecules from Metal Surfaces Using Femtosecond Pulses: A Model Dynamical Study

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The influence of a femtosecond laser pulse on an adsorbate molecule−metal surface system is investigated by considering a time-dependent coupling between the ground- and excited-state potential energy curves using the time-dependent quantum mechanical wave packet approach. It is shown that the probability of desorption is strongly dependent on the duration of the coupling and the image−charge attraction and that it increases with increase in vibrational excitation of the metal−adsorbate bond.

## 1. Introduction

Photoinduced desorption (PID) of molecules from surfaces is being studied with renewed vigor because of the availability of femtosecond (fs) laser pulses.[1−3] Early experiments by Cavanagh and co-workers[4] on Pt(111)/NO and subsequent ones by Murata and co-workers[5] using nanosecond (ns) laser pulses in the UV−visible region showed that the desorbed NO was translationally and rovibrationally hotter than could be accounted for by surface heating or other thermal relaxation processes. Further experiments on Pd(111)/NO,[6] Ag(111)/NO,[7] Cu(111)/NO,[7,8] Pt(111)/$O_2$,[9] and Cu(111)/CO[10] using shorter laser pulses also yielded vibrationally hot desorbed molecules (NO, CO) and in some cases the yield (Y) increased nonlinearly with increase in laser fluence (LF).

Results on PID obtained using ns pulses could be accounted for by a two-state four-step model[11] in the spirit of Menzel−Gomer−Redhead (MGR)[12] and Antoniewicz[13] models. The essential features of the proposed mechanism are the creation of hot electrons by the incident photon, formation of negative ions of adsorbate, and image−charge attraction to the surface resulting in neutralization and desorption. Holloway and co-workers[14] included the electronic motion explicitly in a time-dependent quantum mechanical framework. Saalfrank et al. used a density matrix approach[15] and also a wave packet approach[16] to investigate the PID, in one dimension.

In our earlier work[17] we had examined the possibility of photoinduced desorption in a model Pt−NO system by transferring the wave function corresponding to the ground electronic ground vibrational state of the substrate−adsorbate to the electronic excited-state potential energy surface (PES), which included an electron transfer from the metal to the molecule and the concomitant image−charge[18] interaction. We had assumed a $\delta$-function for the temporal structure of the excitation and had time-evolved the wave packet on the excited-state PES for various time intervals. By considering a $\delta$-function deexcitation to the ground-state PES and time-evolving further, we could compute the desorption probability ($P_{des}$).[19] As expected, $P_{des}$ was found to be a strong function of the residence time ($\Delta t_d$) on the excited-state PES. The experimentally observed $P_{des}$ would correspond not to any particular $\Delta t_d$ but to a distribution of $\Delta t_d$.

Understanding the experimental results obtained using fs pulses rather than ns pulses of equal fluence requires one to go beyond the two-state four-step model discussed above because the fs pulses generate a much larger number density of hot electrons. Under these conditions there is the likelihood of a manyfold repetition of the transfer events between the PES described above, now involving the adsorbate−substrate bond in various stages of vibrational excitation. This is referred to as DIMET[20] (desorption induced by *multiple* electronic transitions) in contrast to the DIET (desorption induced by electronic transition) mechanism proposed earlier.[11] There have also been related efforts to interpret the fs results explicitly in terms of electronic friction.[21]

In an attempt to better understand the fundamental quantum dynamics involved in the PID process, we focus attention here on the temporal shape of the pulse and its influence on the excitation dynamics of the adsorbate−substrate coordinate. Since the electronic motion is relatively fast, it should be adequate to concentrate on the nuclear motion as long as we have a reasonable representation of the coupling between the ground- and excited-state potential energy curves. We present a model study in which the time-dependent coupling is given a temporal shape proportional to that of the (fs) laser pulse. We then solve the coupled nuclear motion problem using time-dependent quantum mechanical wave packet propagation techniques.[22] Such an approach allows for continuous transfer of the system wave function from the ground electronic state to the excited electronic state and back throughout the duration of the interaction. This procedure appears to be similar to a continuous limit of the discrete up-and-down cycling which is the defining characteristic of the DIMET process. Guo and Liu[23] have taken a similar view of the problem but followed the time-dependent perturbation theoretic route without taking into account an explicit time-dependence of the coupling.

The basic methodology and numerical details of our approach are presented in section 2. That is followed by a presentation of results and discussion in section 3 and summary and conclusion in section 4.

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**TABLE 1: Potential Energy Parameters**

| | |
|---|---|
| $D_e$ | 1.08 eV |
| $\alpha$ | 1.708 $a_0^{-1}$ |
| $Z_e$ | 2.83 $a_0$ |
| $W$ | 5.70 eV |
| EA | 0.026 eV |
| $\delta Z$ | 0.15 $a_0$ |

## 2. Methodology

The photodesorption dynamics of an adsorbate−substrate system can be followed by solving the coupled time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\begin{pmatrix}\psi_g\\ \psi_e\end{pmatrix}=\begin{pmatrix}H_g & V_{int}\\ V_{int} & H_e\end{pmatrix}\begin{pmatrix}\psi_g\\ \psi_e\end{pmatrix} \quad (1)$$

where $\psi_g$ and $\psi_e$ represent the wave functions in the ground and excited states, respectively. $H_g$ is the ground-state Hamiltonian

$$H_g = -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial Z^2} + V_g(Z) \quad (2)$$

where $M$ is the mass of the desorbing molecule, $Z$ the desorption coordinate, and $V_g$ the ground-state potential energy (PE) curve. $H_e$ is the excited-state Hamiltonian defined analogous to $H_g$, with $V_e$, the excited-state PE curve taking the place of $V_g$ in eq 2. $V_{int}$ represents the interaction between the ground and excited electronic states of the system. In the absence of any external influence, it would correspond to the nonadiabatic coupling in the diabatic representation and would be $Z$-dependent. In the present case, however, it would represent the consequences of the fs laser pulse interaction with the substrate−adsorbate system, which includes the creation of hot electrons and their interaction with the adsorbate. Since such an interaction would be strongly dependent on the shape of the laser pulse, it is not unreasonable, as an exploratory study, to allow $V_{int}$ to be similar to the shape of the laser pulse.

As an illustrative example we consider

$$V_{int}(t) = A(t)\cos(\omega_p t) \quad (3)$$

where $\omega_p$ is the angular (central) frequency of the laser pulse. We choose

$$A(t) = A_0 \sin^2(\pi t/t_p) \quad (0 \le t \le t_p)$$
$$= 0 \quad (t < 0, t > t_p) \quad (4)$$

where $A_0$ is proportional to the amplitude of the excitation pulse (taken to be unity) and $t_p$ is its duration. Although other shapes such as a Gaussian could have been considered, we do not expect the results to be too strongly dependent on such finer details. In addition, the shape function described in eq 4 has a smooth switch-on-and-off behavior.[24]

We have considered a Morse type of interaction between the metal surface and the center-of-mass of the adsorbate for the ground-state PE curve:

$$V_g = D_e[e^{-2\alpha(Z-Z_e)} - 2e^{-\alpha(Z-Z_e)}] \quad (5)$$

where $D_e$, $\alpha$, and $Z_e$ are the Morse parameters corresponding to Pt−NO interaction and are listed in Table 1. The excited-state PE curve, $V_e$, includes an image−charge interaction and a constant energy term (algebraic sum of the work function ($W$) for Pt(111) surface and the electron affinity (EA) of NO) to describe the state of the negative molecular ion and the positively charged surface, in addition to the Morse curve for the ground-state interaction with the well minimum shifted toward the metal surface by $\delta Z$:

$$V_e = D_e[e^{-2\alpha(Z-Z_e+\delta Z)} - 2e^{-\alpha(Z-Z_e+\delta Z)}] + (W - \mathrm{EA}) - \frac{e^2}{4[Z_{im} + (Z - Z_e)]} \quad (6)$$

**TABLE 2: Choice of $Z_{im}$ Values and the Corresponding Franck−Condon Energy Gaps ($E_{exc}$) and the Excitation Wavelengths ($\lambda$) for the Different Sets of Calculations**

| $Z_{im}$ ($a_0$) | $E_{exc}$ (eV) | $\lambda$ (nm) |
|---|---|---|
| 1.8 | 1.75 | 708 |
| 1.9 | 2.0 | 620 |
| 2.0 | 2.3 | 539 |
| 2.1 | 2.45 | 506 |

Values of $W$, EA, and $\delta Z$ used are also included in Table 1. The value of $Z_{im}$ is chosen differently in different sets of calculations (see below).

At $t = 0$ the wave function $\psi_g$ corresponds to the Morse wave function ($\chi_\upsilon$) for the vibrational state $\upsilon$ of the ground electronic state and $\psi_e = 0$ (0 K approximation). Time evolution of the wave function on the coupled PE curves is followed numerically by solving eq 1 using the second-order differencing scheme:[25]

$$\psi_g(t + \Delta t) = \psi_g(t - \Delta t) - \frac{2i\Delta t}{\hbar} H_g\psi_g(t) - \frac{2i\Delta t}{\hbar} V_{int}(t)\,\psi_e(t) \quad (7)$$

$$\psi_e(t + \Delta t) = \psi_e(t - \Delta t) - \frac{2i\Delta t}{\hbar} H_e\psi_e(t) - \frac{2i\Delta t}{\hbar} V_{int}(t)\,\psi_g(t) \quad (8)$$

Each time step $\Delta t$ corresponds to 0.027 fs. The spatial propagation of the wave function is accomplished using the fast Fourier transform (FFT) algorithm. The spatial grid consisted of 1024 grid points with ($Z_{min}$, $\Delta Z$, $Z_{max}$) = (2.0, 0.02, 22.46) $a_0$.

Four different excited-state PE curves (characterized by four different image plane locations ($Z_{im}$ values)) are considered, and for each one of them the excitation frequency corresponding to the Franck−Condon energy gap is chosen. The different values of $Z_{im}$ used and the corresponding excitation wavelengths are mentioned in Table 2.

During the duration of the off-diagonal coupling, the dynamics is followed by solving eq 1. After the interaction is over, the time evolution of the wave function is carried out only on the ground-state PE curve. For calculating the desorption probability, $P_{des}$, we consider a separation point $Z_d$ on the grid, beyond which the molecules are treated as desorbed. We have taken $Z_d = Z_e + 4a_0$ in our calculation. We have used a large enough grid (1024 grid points) to ensure that even after a long time evolution portions of the wave packet do not reach the grid edge and that $P_{des}$ converges. At the end of the time evolution $P_{des}$ is computed according to the following expression:

$$P_{des} = \int_{Z_d}^{Z_{max}} \psi(z, t_f)\,\psi^*(z, t_f)\mathrm{d}z \quad (9)$$

where $Z_{max}$ is the edge of the grid and $t_f \gg t_p$ is a final time when $P_{des}$ has approached its asymptotic limit.

## 3. Results and Discussion

We consider the substrate−adsorbate system in its $\upsilon = 0$ state of the ground electronic state subjected to $V_{int}$ defined in eq 3

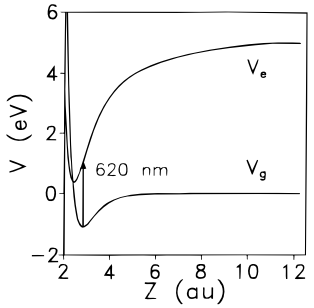


**Figure 1.** Potential energy curve for the ground and excited states of a model Pt−NO system for $Z_{im} = 1.9\ a_0$. The Franck−Condon excitation wavelength is included.

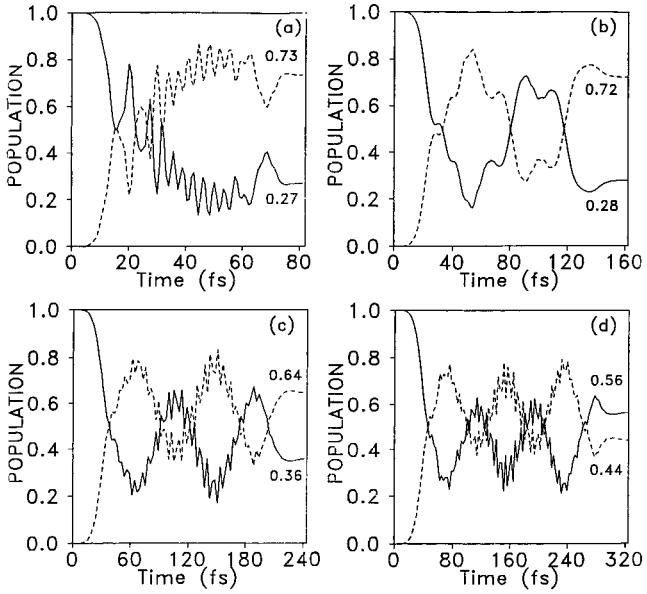


**Figure 2.** Population variation with time in the ground and excited states for $V_{int}$ (eqs 3 and 4) with $t_p$ = (a) 80.80, (b) 161.62, (c) 242.44, and (d) 323.26 fs for initial $v = 0$ of the substrate−adsorbate coordinate. The solid line shows the population of the ground state and the dashed line that in the excited state.

with $\omega_p$ corresponding to $\lambda = 620$ nm. The excited-state PE is defined in eq 6 with $Z_{im} = 1.9\ a_0$. The resulting PE curve, along with the ground-state PE curve, is illustrated in Figure 1. At $t = 0$, the wave function is located completely in the ground electronic state. With increase in time, more and more pieces of the wave function arrive in the excited state, while at the same time some of them get deexcited with the result that the population in the ground and excited states fluctuates with time,[26] as can be seen from Figure 2 for four different values of $t_p$ (see eq 4). At the end of the time-dependent perturbation, population exchange between the states ceases and the populations on both the states become steady in the present model. To focus attention here on the desorption consequences due to the inherent time dependence of $V_{int}$, we have excluded any desorption from population trapped in the excited state that could subsequently decay into desorptive channels on the electronic ground state PE curve via other relaxation processes possibly operative in nature but not in our limited model. Thus the effective population that contributes to the ("stimulated" as opposed to "spontaneous") desorption probability has arrived on the ground electronic state only as a result of $V_{int}$, and once this interaction is over, no further accumulation there is allowed. The resulting probability density distribution on the ground electronic state after the coupling is over is plotted in Figure 3

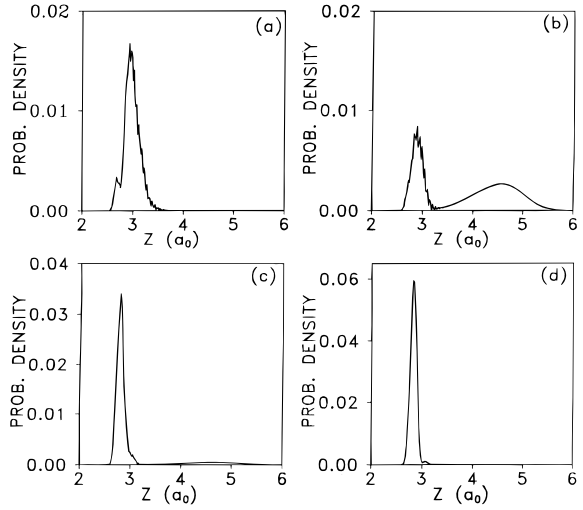


**Figure 3.** Probability density distribution on the ground electronic state (after the coupling is over) for different values of $t_p$ = (a) 80.80, (b) 161.62, (c) 242.44, and (d) 323.26 fs for initial $v = 0$ and $Z_{im} = 1.9\ a_0$.

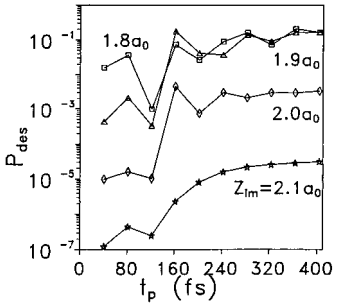


**Figure 4.** $P_{des}$ as a function of $t_p$ values for different $Z_{im}$ values for initial $v = 0$.

for the different values of $t_p$. Values of $P_{des}$ computed using eq 9 for four different excited states characterized by four different values of $Z_{im}$ are plotted in Figure 4. It is seen that $P_{des}$ is strongly dependent on the duration ($t_p$) of the coupling and also on the choice of $Z_{im}$. For $Z_{im}$ values of 1.8, 1.9, 2.0, and 2.1 $a_0$ $P_{des}$ varies over a wide range: $10^{-2}$−0.20, $10^{-4}$−0.16, $10^{-6}$−$10^{-2}$, and $10^{-4}$−$10^{-7}$, respectively. This is physically understandable since a smaller $Z_{im}$ implies a larger force on the admolecule while in the intermediate state and larger force would imply larger desorption probabilities. For a given $Z_{im}$, $P_{des}$ increases in general with increase in $t_p$. However, there are local fluctuations in the curve and they correspond approximately to the vibrational period on the excited state (∼60 fs).

As an illustrative example, for $Z_{im} = 1.9\ a_0$ and $t_p = 80.80$ fs, we have examined the effect of vibrational excitation in the adsorbate−substrate mode on $P_{des}$. The results shown in Figure 5 indicate clearly that $P_{des}$ increases with increase in $v$ in keeping with the expectations of the DIMET mechanism.

Finally it is informative to put the present results into some perspective with past work in which the physical mechanism underlying the desorption process was modeled explicitly in terms of inelastic resonance scattering of hot electrons[3,17,27] rather than implicitly in terms of a parametrized time-dependent trial function such as that given by eqs 3 and 4. As mentioned in the Introduction, the resonance scattering model presumed instantaneous transfer of wave function from the ground-to excited-state potential, propagation on the excited state for some time interval $\Delta t_d$, and then instantaneous return to the ground-state potential. To properly account for the probability of

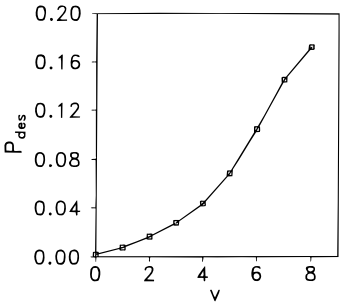


**Figure 5.** $P_{des}$ values for different initial vibrational ($v$) states of the surface−admolecule bond for $t_p = 80.80$ fs and $Z_{im} = 1.9\ a_0$.

survival of the resonance state, the $\Delta t_d$-dependent desorption probability ($P_{des}(\Delta t_d)$) was averaged over all time intervals weighted by the exponential survival probability, resulting in the desorption probability that would be observed:

$$P_{des} = \langle P_{des}(\tau_R)\rangle = \frac{1}{\tau_R}\int_0^\infty d(\Delta t_d) e^{-\Delta t_d/\tau_R} P_{des}(\Delta t_d) \quad (10)$$

where $\tau_R$ is the mean lifetime of the temporary negative ion resonance state.[27] In effect, the "sudden-switching-with-exponential-averaging" procedure plays the role of a time-dependent coupling between ground and excited states in which the principal time-dependent feature is that the coupling is turned on for a time interval of order $\tau_R$. The same job is fulfilled here by the envelope function $A(t)$ given by eq 4, where $t_p$ substitutes for $\tau_R$. It is for this reason that the desorption probability as a function of $t_p$ (with various $Z_{im}$ values) curves shown in Figure 4 here are qualitatively similar to the desorption probability versus $\tau_R$ curves presented elsewhere.[27] The consequence of the additional $\cos(\omega_p t)$ modulation of the off-diagonal interaction in eq 3 is most apparent as the "oscillatory fine structure" in the population versus time plots in Figure 2 and, as such, has only a secondary role in determining either the asymptotic long time population in either state or the ultimate desorption probabilities.

## 4. Summary and Conclusion

We have initiated an investigation of the influence of fs laser pulses on molecules adsorbed on metal surfaces by considering a time-dependent coupling between the ground and excited states of adsorbate−substrate interaction. We have considered a simple $\sin^2$-shaped coupling and shown that the desorption probability, in general, increases with increase in the duration of the coupling. $P_{des}$ increases with decreasing $Z_{im}$, for a given $t_p$. $P_{des}$ increases with increasing vibrational excitation in the substrate−adsorbate coordinate, in keeping with the expectations of the DIMET mechanism.

Last, we have presented a narrative that demonstrates the complementary relation between the results of the present model study and past desorption predictions based on the explicit physical mechanism of resonant inelastic scattering of energetic hot electrons.

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