

APPENDIX A

Theoretical formalism of adsorbate desorption induced by ultrafast pulses on metal surfaces

The theory of ultrafast laser-induced chemical reactions on metal surfaces is still under development, nevertheless it is beneficial to review current theory in explaining this emerging “femtochemistry” field. In particular, the desorption of adsorbates from metal surfaces has been studied for about a decade, both experimentally and theoretically. Theories based on inelastic scattering from nonthermal surface electrons have been used to explain this unconventional desorption process. Furthermore, as was shown experimentally in chapter III and IV, non-thermal surface electrons also play an important role in excitation of chemisorbed states, and molecular vibrational modes. Therefore, a brief review of current theories of desorption can give insight to help understand various possible explanations.

A.1 Desorption induced by electronic transition (DIET)

Conventional thermal-driven chemical reactions on metal surfaces are thought to be a process of the adsorbate molecules overcoming the reaction energy barrier required for desorption, by progressively acquiring energy from the surface lattice phonons. However,

femtochemistry on metal surfaces cannot be explained using traditional theories. New theories have been proposed to explain the underlying mechanism of this new phenomenon.

When an energetic electron inelastically scatters with a molecule in the gas phase, the probability of vibrationally exciting the molecule through electron scattering is well known to be greatly increased if the incident electron can be trapped into a “shape resonance”. This shape resonance corresponds to a particular orbital of the gas-phase molecule that forms a temporary negative molecular ion [117, 118, 119, 120, 121]. This can be explained by “Franck-Condon” principle [122]: When an electron is trapped into a molecular orbital, the “Born-Oppenheimer” (BO) or “Adiabatic” approximation [123] can be applied. Under this approximation, atomic motion is considered to be “frozen” while the electronic transition is occurring; i.e., the motion of electrons is much faster than the motion of the atomic nuclei. The sudden change of the molecule’s Hamiltonian due to this excited state transition instantaneously effects the forces on the nuclei, causing the molecule to vibrate.

This theory can be used to describe the process of adsorbate desorption from metal surfaces via intense ultrafast pulses. An intense laser field generates hot surface electrons on a metal surface, and these electrons can tunnel into the unoccupied states of the adsorbates, initiating the process of desorption.

The effectiveness of resonant excitation depends on two important factors. First, the incident electrons must be trapped in a “bond-significant” orbital; that is, one whose occupancy provides new forces on the atomic constituents. In this way, the equilibrium geometry of the negative ion differs from that of the original neutral target. It is very important that the electron be trapped in order to efficiently transfer energy via Franck-

Condon excitation. Under these conditions, the excited potential energy surface (PES) of the atomic space, modified by the trapped electrons, sets the atoms in motion. In contrast, pure inelastic scattering between energetic electrons and atoms does not transfer enough energy from the electron to the atom because the atom is much heavier than the electron in weight.

Second, the effectiveness of this resonant bond excitation depends strongly on the lifetime of the resonant negative-ion state relative to a characteristic time scale for “significant” nuclear motion on the excited PES. For example, for adsorbate desorption from metal surfaces, the highest possibility of molecular desorption occurs when the adsorbate-metal bond is at its point of greatest compression or expansion. In this situation, the lifetime of the trapped ion will be close to one-half of the vibrational period of the adsorbates.

A.1.1 Resonant excitation by non-thermal surface electrons

On metal surfaces, nonthermal surface electrons created by ultrafast pulses become the equivalent of energetic incoming electrons to the molecules in the gas phase. Similar to conventional thermal surface chemistry, the temperatures of the surface electrons and the phonons (lattice) reach an equilibrium at all times. In femtochemistry, energy from the ultrafast pulses heats the surface electrons within the first picosecond, while the motion of the surface lattice is slow. Thus, the lattice remains unperturbed some picoseconds after the excitation. Figure A.1 is a schematic diagram showing the energy level of an adsorbate that is adsorbed onto a metal surface. The highest occupied molecular orbital (HOMO) of the adsorbate is partially filled by electrons, up to the Fermi-level, while the lowest unoccupied molecular orbital (LUMO) of the adsorbate is left unfilled. In general, there is an energy

barrier between the adsorbate and the metal surface, which is created by the space-group symmetry broken on the metal surface. This barrier prevents the metal's surface electrons freely propagating into the adsorbate orbitals [123]. Before laser excitation, the adsorbate is in equilibrium with the metal surface and resides in the ground state PES of the system.

When an ultrafast pulse hits the metal surface, individual surface electrons will adsorb one photon from the ultrafast pulse, raising their kinetic energy by $h\nu$. Since metals have no band gap, electrons can exist at a range of energies above the Fermi-edge (from ε_{Fermi} to $\varepsilon_{Fermi} + h\nu$), as shown in Fig. A.1. These excited electrons produce a photoelectron current $\equiv j_{el}(\mathbf{k}(\varepsilon_{in}; h\nu))$ from within the surface which is incident upon the adsorbed molecules. If the energy level of the LUMO state of the adsorbates falls within this energy range, the nonthermal surface electrons, having acquired sufficient energy, can transfer (or tunnel) to the adsorbate molecules by the process of resonance scattering. Typically, the incident electrons will reside in this resonance state for a time τ_R , and then scatter back into an unoccupied conduction band state with energy $\varepsilon_f \leq \varepsilon_i$, leaving the adsorbate excited with a net energy $\Delta\varepsilon = \varepsilon_i - \varepsilon_f$.

When an electron scatters into the LUMO state, the adsorbates' Hamiltonian changes suddenly. Thus, the adsorbates are excited from the ground state PES to an excited state PES. The BO approximation tells us that the electronic state of the adsorbate system determines the PES for the adsorbate nuclei. Therefore, when an extra electron couples to the LUMO state of the adsorbate, the adsorbate is suddenly excited to an excited-state PES, and atomic forces subsequently cause the nuclei of the adsorbates to move. The results is atomic motion, mediated by non-thermal electrons, can lead to a cleav-

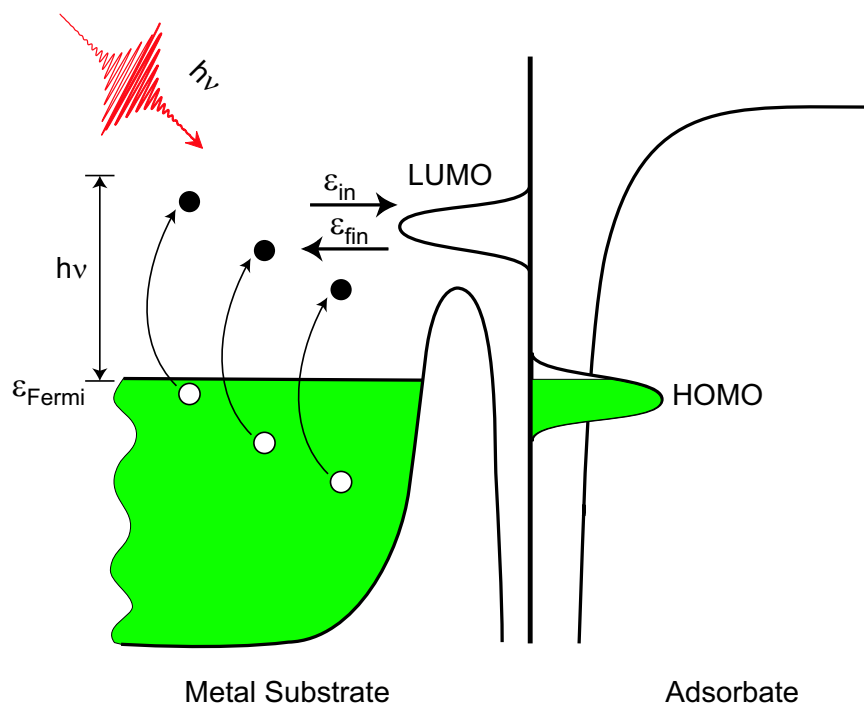


Figure A.1: Energy level diagram showing that the non-thermal electrons are energized rapidly by an intense ultrafast pulse. These “hot” electrons could scatter into the LUMO state of the adsorbates to transfer energy to excite the molecular motions through Franck-Condon excitation scheme. (figure reproduced from Ref. [79])

age of the bond between the adsorbates and the surface, ultimately leading to desorption. This desorption scheme is generally called “Desorption Induced by Electronic Transition” (DIET).[124, 125]

A schematic diagram of the DIET process, depicted in Fig. A.2, shows the PES (one-dimensional curve for simplicity) associated with the electronic ground and excited states. There are two scenarios under which DIET can occur, depending on the nature of the adsorbates’ excited-state PES.

Fig. A.2(a) depicts the most straight forward DIET process, in which the adsorbates enter a repulsive excited-state PES. After the adsorbate enters the excited-state PES, characterized by an repulsive potential V_{excite} , the adsorbate is accelerated on an outward trajectory. Under this scenario, three outcomes are possible. The first case (and most typical) is a rapid relaxation of the adsorbate, falling back onto the ground-state PES V_0 , with a slightly displaced from the equilibrium position z_0 . The adsorbate has picked some kinetic energy by temporally residing on V_{excite} , but not enough to overcome the energy barrier for desorption. Classically, this means that relaxation occurs prior to the adsorbates’ trajectory arriving at the diabatic curve crossing point $z = z_c$. The second possible outcome, and the major desorption channel for the adsorbate, occurs when the adsorbate resides on V_{excite} long enough to cross the point z_c , later relaxing back to V_0 with kinetic energy $\varepsilon^* = V_{excite}(z_0) > \varepsilon_0^{inf}$, i.e., enough to overcome the energy barrier for desorption. The final case, which is rare, occurs when the adsorbate stays on the excited-state PES until complete desorption happens.

Another scenario of the DIET process, which is strongly dependent on the adsorbate

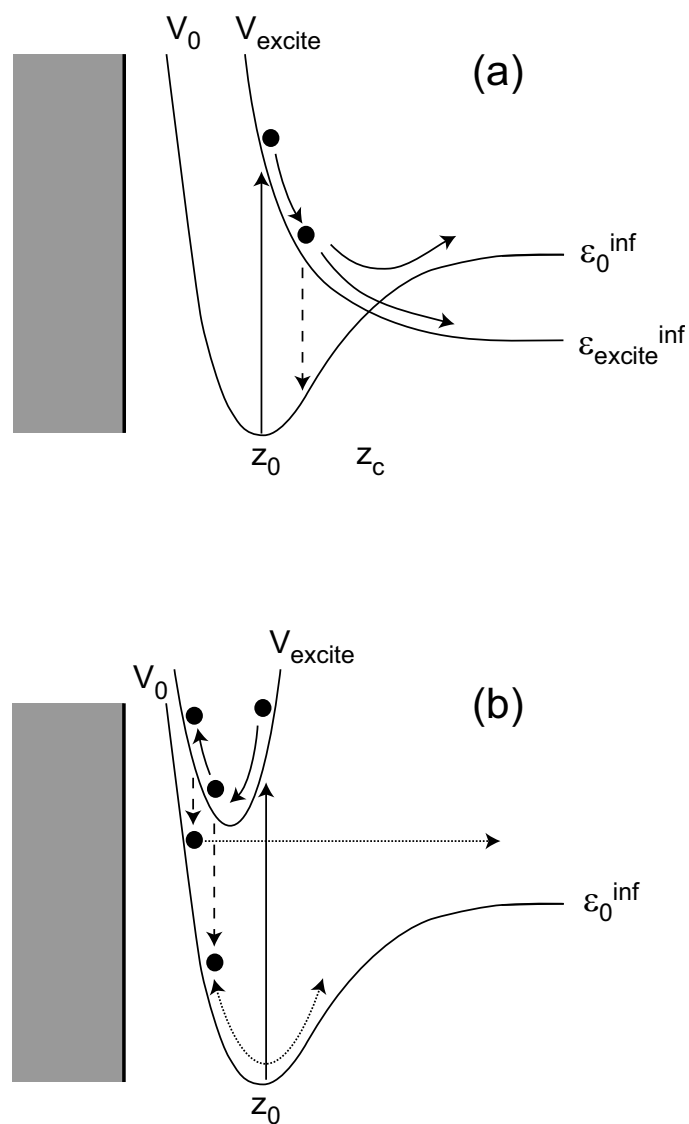


Figure A.2: Potential curves illustrating the process of Desorption Induced by Electronic Transition (DIET). (a) Intra-molecular electronic excitation involving bound-to-repulsive excitation; (b) Intra-molecular electronic excitation involving attractive intermediate state mediation. (figure reproduced from Ref. [79])

motion over V_{excite} , is illustrated in Fig. A.2(b). Here the excited-state PES is more closely bonded to the surface than the ground-state PES. When this happens, the adsorbate will be pulled towards the metal surface following the electronic transfer. Consequently, the initial accelerated nuclear motion is directed inwards such that when the excited state decays back to the ground state (usually within a fraction of a vibrational period), not only has the adsorbate acquired kinetic energy but, perhaps more importantly, it is returned high up on the repulsive wall of the ground-state PES, with a compressed bond between surface and adsorbate. Depending upon the parameters, while the adsorbate is in the intermediate excited-state PES, it may or may not obtain sufficient kinetic energy to desorb once back in the ground-state PES. Both situations (successful desorption and remaining adsorbed) are shown in Fig. A.2(b).

A.1.2 Desorption probability

The energy-resolved production rate for adsorbates with total energy ε , due to resonance scattering by the non-thermal surface electrons is written as $d\dot{N}(\varepsilon; \tau_R, h\nu)/d\varepsilon$. The non-thermal surface electrons are scattered from state \mathbf{k}_i to state \mathbf{k}_f , with energy ε_i and $\varepsilon_f = \varepsilon_i - \varepsilon \geq \varepsilon_{Fermi}$, respectively [79]. This give us

$$\frac{d\dot{N}}{d\varepsilon}(\varepsilon; \tau_R, h\nu) = \sum_{\mathbf{k}_i, \mathbf{k}_f} j_{el}(\mathbf{k}_i; h\nu) \sigma_{Tot}(\varepsilon_i(\mathbf{k}_i); \varepsilon_f(\mathbf{k}_f); \tau_R) \delta(\varepsilon_i - \varepsilon_f - \varepsilon) \quad (\text{A.1})$$

In this expression, τ_R is the propagation time the adsorbate spends on the excited-state PES $V_-(z)$ before decaying back to the ground-state PES $V_a(z)$. $j_{el}(\mathbf{k}_i; h\nu)$ is the flux distribution of non-thermal surface electrons incident upon the adsorbates. The flux is characterized by the wave-vector \mathbf{k}_i and depends on the laser photon energy $h\nu$. $\sigma_{Tot}(\varepsilon_i(\mathbf{k}_i); \varepsilon_f(\mathbf{k}_f); \tau_R)$ is the total inelastic resonance scattering cross-section, which depends on the incident en-

ergy ε_i , and exit energy ε_f of the electron, and the propagation time τ_R . Equation A.1 can be simplified under some reasonable assumptions, (concerning relatively weak optical excitation [79]), to

$$\frac{d\dot{N}}{d\varepsilon}(\varepsilon; \tau_R, h\nu) \approx Q_{Res}(\varepsilon, h\nu)P(\varepsilon, \tau_R) \quad (\text{A.2})$$

where $P(\varepsilon, \tau_R)$ is the total probability distribution for exciting the molecule with energy ε . A graphical description of $P(\varepsilon, \tau_R)$ is shown in Fig. A.3. Q_{Res} is the electronic factor, which is assumed to be slowly varying over the energy spread of $P(\varepsilon, \tau_R)$. Here, the electronic factor Q_{Res} is approximated to be a constant, and includes all the averaged effects of the incident flux j_{el} and the scattering cross-section σ_{Tot} that occur during the scattering process. The distribution $P(\varepsilon, \tau_R)$ can be evaluated using various microscopic theories. The ‘‘Gaussian wavepacket model’’ is commonly used as it provides a physically intuitive picture of the desorption mechanism using features of classical mechanics while retaining many quantum attributes.

Using the ‘‘Gaussian wavepacket model’’, the distribution $P(\varepsilon, \tau_R)$ can be written as [126]

$$P(\varepsilon; \tau_R) = \frac{1}{\Delta(\tau_R)\sqrt{2\pi}} \exp \left[-\frac{1}{2} \left(\frac{\varepsilon - \varepsilon_f(\tau_R)}{\Delta(\tau_R)} \right)^2 \right] \quad (\text{A.3})$$

with

$$\Delta(\tau_R) \equiv \bar{u}V'_a(z_{\tau_R})[1 + (\omega\tau_R)^2]^{1/2} \quad (\text{A.4})$$

and

$$\varepsilon_f(\tau_R) = \frac{p_{\tau_R}^2}{2M} + V_a(z_{\tau_R}) \quad (\text{A.5})$$

Equation A.4 shows that the width of the energy distribution after the wavepacket returns

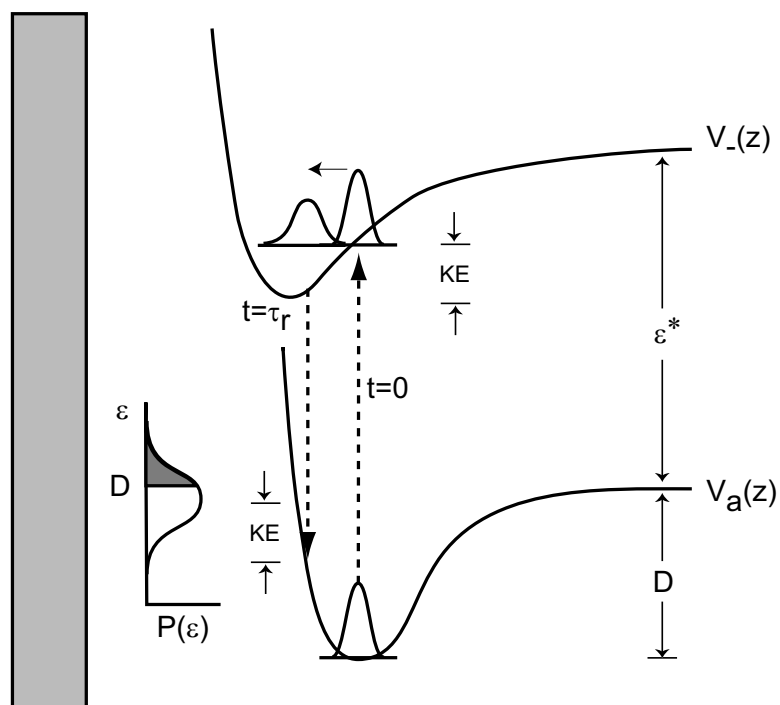


Figure A.3: Potential energy curves of center-of-mass translational motion of the chemisorbed ion (charge transfer from surface) with respect to the surface, showing wavepacket propagation throughout the time sequence involving the negative-ion LUMO resonance. The distribution of the final adsorbate states, between vibrationally excited bound (white) and desorptive continuum states (black) is shown as $P(\varepsilon)$ versus ε . (figure reproduced from Ref. [79])

to the ground-state PES $V_a(z)$ at τ_R is determined by the combination of $\bar{u} = (\hbar/2M\omega)^{1/2}$, the spread of the original ($t = 0$) oscillator probability distribution V'_a , the slope of V_a at the point of return, and the additional width acquired while propagating on V_- .

The desorption probability for the adsorbates can then be determined by integrating $P(\varepsilon; \tau_R)$ from the desorption barrier D to infinity. This is

$$P_{des}(\tau_R) = \int_D^{\hbar\nu} P(\varepsilon; \tau_R) d\varepsilon \quad (\text{A.6})$$

which for $\hbar\nu \gg D$ reduces to

$$P_{des}(\tau_R) \simeq 0.5 \left[1 - \text{erf} \left(\frac{D - \varepsilon_f(\tau_R)}{\sqrt{2}\Delta(\tau_R)} \right) \right] \quad (\text{A.7})$$

A.2 Desorption induced by multiple electronic transition (DIMET)

The desorption rate $P_{des}(\tau_R)$ of the adsorbates depends on the propagation time τ_R , as the adsorbates undergo motion on the excited-state PES in this time scale to obtain kinetic energy to overcome the desorption barrier D . In general, the propagation time τ_R can be interpreted as the time that non-thermal electrons spend in the LUMO state of the adsorbate, and is in general very short. Therefore, most adsorbates will not be able to obtain enough kinetic energy to escape from the well upon returning to the ground-state PES $V_a(z)$. This does not explain the non-traditional exponential increase in desorption with ultrafast laser excitation.

In the conventional DIET scheme, most of the adsorbates will not contribute to the desorption yield as not enough kinetic energy is generally obtained in a single excitation process. In DIMET [11, 127], on the other hand, adsorbates could be re-excited before its kinetic energy gained through the previous DIET process is totally relaxed, due to the high

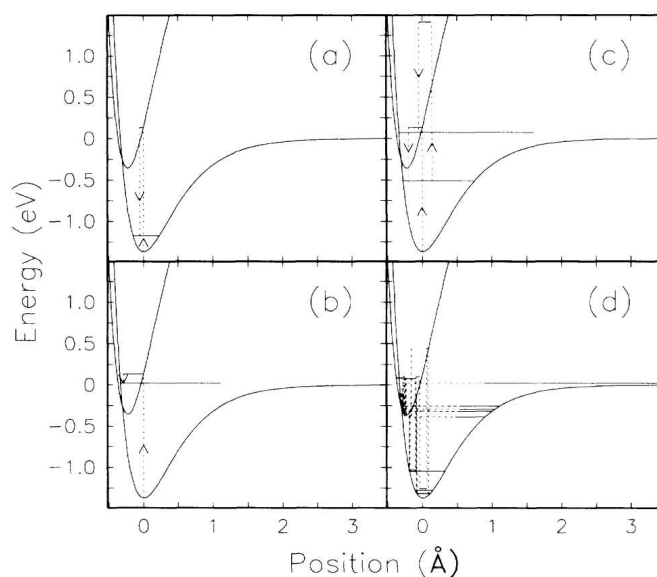


Figure A.4: Trajectories for motion on the ground and excited PES. The dotted lines represent the total energy of the adsorbate complex, with vertical segments arising from Franck-Condon transitions and horizontal segments from conservative motion on a given PES. (a)(b) Trajectories displayed associated with a single-excitation DIET process. (c)(d) Trajectories for the multiple-excitation DIMET process. (figure reproduced from Ref. [11])

concentration of non-thermal surface electrons. This situation is shown in Fig. A.4(c) and (d). The adsorbate makes another Franck-Condon transition, this time from a vibrationally excited level of the ground-state PES. The additional energy associated with the vibrational excitation allows the adsorbate to desorb more easily previously discussed excitations. However, if the excitations are separated by more than the lifetime of the adsorbate-surface vibration, the DIMET mechanism is simply several single DIET excitations, which will not lead to enhancement of the desorption yield.