

# *Laser-Excited Hot-Electron Induced Desorption*

The quest for femtochemistry provided a guiding motivation for many researchers [1,2] far in advance of the award of the 1999 Nobel Prize in Chemistry to Ahmed Zewail “for his pioneering investigation of fundamental chemical reactions, using ultra short laser flashes, on the time scale on which the reactions actually occur” [3]. The rich array of possibilities that femtochemistry potentially offered within the domain of surface-science-related phenomena was the driving force for a very significant research effort, starting in the mid 1980s, involving core members of the Surface Dynamical Processes Group within the Surface Science Division (SSD). This group was first part of the Center for Chemical Physics, then the Center for Atomic, Molecular, and Optical Physics, and most recently the Chemical Science and Technology Laboratory. The initial desorption results with pulsed laser-induced surface processing reported in 1988 [4] strongly suggested that an entirely new physical mechanism, different from that operating in gas phase femtochemistry, was required to account for the laser-induced molecular processes on solid surfaces. Stimulated by this discovery, a transient quantum wave packet model was conceived, developed, and first reported in the 1990 paper *Laser-excited hot-electron induced desorption: a theoretical model applied to NO/Pt(111)* [1]. In this model, laser-excited hot electrons produced within the solid are inelastically scattered from the surface chemical system via resonance formation of a temporary negative ion. This picture has become a standard paradigm for modeling, and hence understanding, almost all hot-electron-induced molecular processes at surfaces involving not only laser excitation, but also STM (Scanning Tunneling Microscope)-, tunnel junction-, and electrochemically-produced hot electrons. For this reason among others, the consequences of this coupled theoretical and experimental research are expected to have an active and lasting impact on our understanding and control of many of the most important electron-induced surface processes of chemical significance [5].

The decade of the 1970s was filled with the excitement accompanying the initial development, utilization, and theoretical interpretation of surface-sensitive spectroscopic probes which enabled a quantum mechanical description of clean and composite surfaces. Our ability to determine not only the electronic state of the surface

[6], but also the properties characterizing the quantized nuclear motion of the bound constituent atoms, as revealed in vibrational spectroscopies [7], were opening up entirely new vistas in conceptualizing and understanding surface properties and processes. Once the machinery for static surface characterization was in place, it was natural to address next the intellectual and technical challenges presented in surface dynamics. This was understood to mean the observation and control of time-dependent fundamental processes that are the atomic-level (both spatial and temporal) building blocks determining the rates for excitation, decay, growth, aging, chemical reactions, catalysis, etc. Bond-selective nonequilibrium placement of energy within a molecular system, subsequent energy flow and redistribution, intentional use of the out-of-equilibrium state, and production of far-from-statistical product distributions and branching ratios became the new goals.

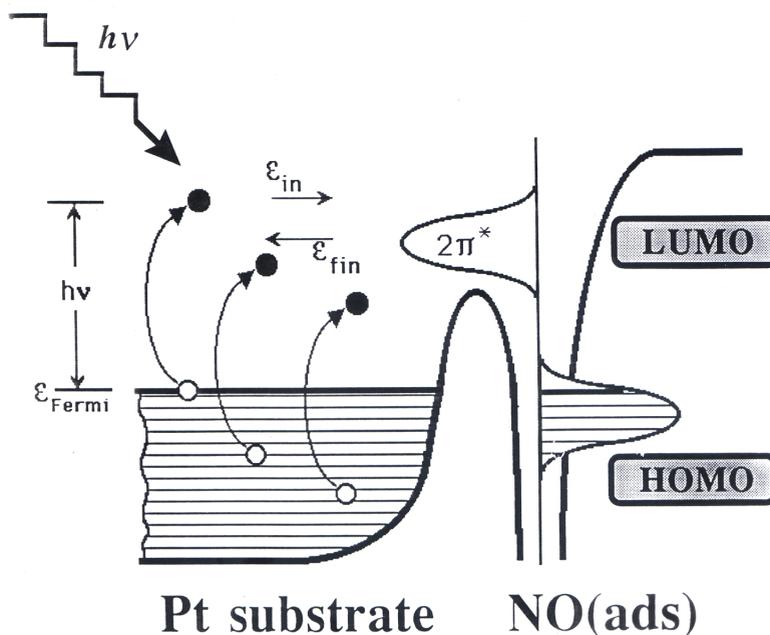
In the late 1970s, Rich Cavanagh came to NBS as an NRC Postdoctoral Fellow working with John Yates, initially on infrared and neutron surface vibrational spectroscopy and thermal desorption. About the same time, David King joined the laser chemistry group headed by John Stephenson to study time-dependent, laser-assisted molecular processes in the gas phase. A propitious collaboration was initiated between Cavanagh and King which produced the first-ever quantum-state-specific (translational, vibrational, and rotational) energy distribution measurements of molecules thermally desorbed from metal surfaces (NO/Ru(001)) in which laser excited fluorescence (LEF) techniques were used to deduce the internal state population distributions [8]. In early 1988, new NRC Postdoctoral Fellows Steve Buntin and Lee Richter joined Cavanagh and King to study “fast” pulsed laser-induced desorption, again using LEF to interrogate the desorbed molecules. This combination of laser applications, both as an active participant in the process under study (desorption) and also as a diagnostic tool (energy distributions), was crucial in the development of femtosecond surface chemistry [9,10]. In their “paradigm-establishing” 1988 note in *Physical Review Letters* [4], convincing evidence was presented which suggested that, contrary to expectations, desorption was caused not by local laser heating of either the substrate lattice or by the direct pumping of the adsorbate-surface bond, but instead by some as yet unknown mechanism involving electrons

that were “super-heated” far in excess of the surface temperature. As more fully understood later, the degree of excess electron heating is very dependent on the temporal width of the incident laser pulse; tens of femtosecond pulses produce much hotter electrons (but for a shorter length of time!) and, as a result, cause different surface reactions than do pico-to-nanosecond pulses with equal energy content [9,11]. This distinction has turned out to be very important in the pursuit of surface femtochemistry [9,10]

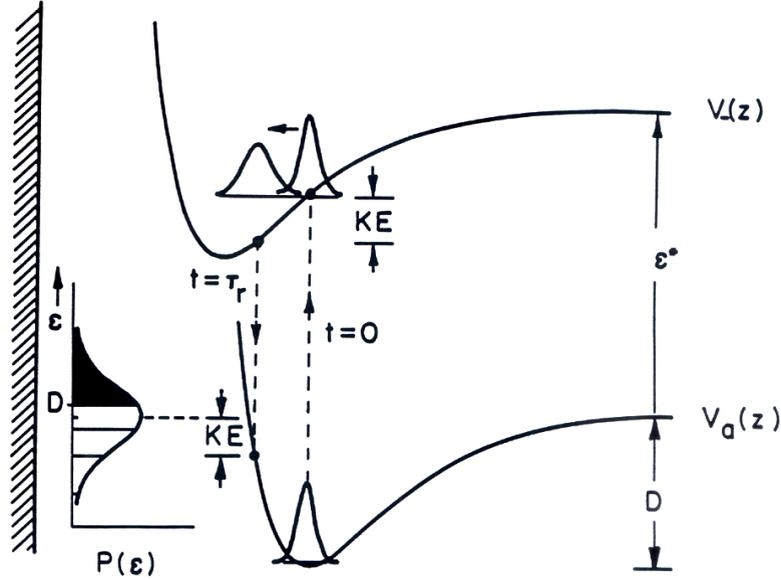
From the theoretical point of view, Bill Gadzuk had for a long time been keenly interested in the electronic properties of adsorbed systems [6]. By the 1980s, his considerations had also shifted towards problems in surface dynamics, particularly ones involving atomic motion triggered by electron charge transfer [12] and resonance scattering [13] involving atoms on surfaces. At the time of the first laser desorption experiments, he was working with John Yates (formerly from the SSD, then and now at the University of Pittsburgh [14]) on what appeared to be resonant electron stimulated desorption [15]. Together with Charles Clark, he developed a model that explained observations from Yates’ group showing a highly sensitive dependence of the desorption yield of NO/Pd(111) on the energy of the incident exciting electron beam, exactly in the fashion of a hot-electron resonant desorption process [16]. Since

the model did not care how the energetic or hot electrons got “hot,” it was as applicable to the laser-induced hot-electron desorption phenomena under study experimentally by Buntin et. al [4] as to the external electron-beam experiments of Yates’ group [15]. With this realization, it was relatively easy to work the ESD theory [15,16] into a theory for laser desorption, an exercise which produced the 1990 paper [1] and later refinements [2].

The proposed optically driven non-thermal desorption version of the general hot-electron model unfolds in the following way. The incident photon pulse excites a non-equilibrium continuous distribution of hot electrons with energies in the range  $\epsilon_{\text{Fermi}} < \epsilon_{\text{in}} < \epsilon_{\text{Fermi}} + h\nu$  where  $\epsilon_{\text{Fermi}}$  is the Fermi level of the substrate and  $h\nu$  the photon energy, as illustrated in Fig.1. This results in a transient flux of hot electrons incident upon the surface from within. For those photoexcited electrons resonant with the lowest unoccupied “level” of the adsorbate (labeled as the  $2\pi^*$  orbital for NO/Pt), the incident electron with energy  $\epsilon_{\text{in}}$  may hop onto the adsorbed NO, reside in this resonance for a time  $\tau_{\text{R}}$ , and then scatter back into an unoccupied conduction band state with energy  $\epsilon_{\text{fin}} \leq \epsilon_{\text{in}}$ , leaving behind some part of the adsorption system excited with energy  $\epsilon = \epsilon_{\text{in}} - \epsilon_{\text{fin}}$ . With regards to the NO-surface interaction, labeled  $V_{\text{a}}(z)$  in Fig.2, when the incident electron becomes trapped in



**Fig. 1.** Energy level diagram for inelastic hot electron scattering through the lowest unoccupied molecular orbital (LUMO) resonance associated with the adsorbed molecule, also showing the highest occupied molecular orbital (HOMO) resonance level.



**Fig. 2.** Schematic potential energy curves for center of mass translational motion of adsorbed neutral and negative ion species with respect to the surface, showing wavepacket propagation throughout the time sequence involving the negative ion resonance. The distribution of final adsorbate states between vibrationally excited bound and desorptive continuum states is shown as  $P(\epsilon)$  versus  $\epsilon$ .

the  $2\pi^*$  resonance, an additional ionic attraction is turned on, resulting in an augmented negative ion/surface potential labeled  $V_-(z)$ . The desired attribute is that the intermediate state is one in which attractive forces are applied to the  $\text{NO}^-$ , thus requiring different equilibrium geometries for the two charge states.

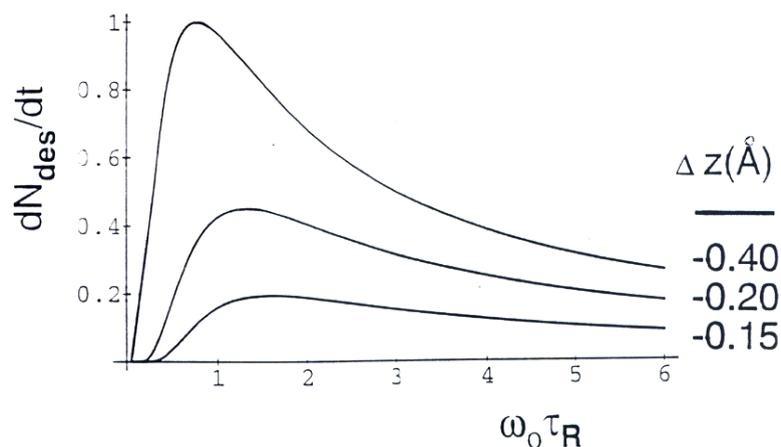
With these thoughts in mind, it was hypothesized that the actual resonance desorption event occurs in the following way. Upon capture of the incident electron in the  $2\pi^*$  orbital,  $\phi_0$ , the ground state wavepacket characterizing the nuclear motion of the adsorbed NO, suddenly finds itself as  $\phi(t)$ , a time-evolving non-stationary state on  $V_-(z)$ , as in a Franck-Condon transition, and thus accelerates inwards towards the surface. After a time interval  $\tau_R$  = the negative ion resonance lifetime, the trapped electron on  $\text{NO}^-$  departs, and the moving displaced and distorted wavepacket is returned to  $V_a(z)$ , possibly on the steeply repulsive inner wall, again as a Franck-Condon transition, but this time involving the projection of a moving initial state wavepacket on both the discrete bound and continuum desorptive states of  $V_a(z)$ . The theory established that the translational energy distribution of excited states resulting from this sequence of electronic transitions is given by:

$$P(\epsilon; \tau_R) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt' e^{i\epsilon t'} \langle \phi(t'=0; \tau_R) | \phi(t'; \tau_R) \rangle$$

which is the Fourier transform of the time-dependent overlap of  $|\phi(t'=0; \tau_R)\rangle$ , the state initially prepared on  $V_a$  at  $t = \tau_R$  after experiencing the forces on the negative

ion, with  $|\phi(t'; \tau_R)\rangle$  the subsequent neutral state which time evolves on  $V_a$ . Theoretical methods for evaluating such expressions using intuitively straightforward semiclassical Gaussian wavepacket dynamics were available at that time and were incorporated into the theory [13]. The desorption or bond-breaking probability per resonance event  $\equiv P_D(\tau_R)$  is given by the integral over those states with energy greater than  $D$ , the desorption energy as represented by the area under the filled-in region of the final state distribution labeled  $P(\epsilon)$  in Fig. 2. As is apparent, the dynamics on  $V_-(z)$ , the intermediate state potential energy curve, can easily lead to a substantial electron-assisted desorption probability.

The desorption rate, which is in principle a measurable quantity of importance, is proportional to the product of  $P_D(\tau_R)$  multiplied by the rate of electron capture into the resonance which, by microscopic reversibility equals  $1/\tau_R$ , the decay rate or inverse resonance lifetime. The theory provided relationships between the independent parameters defining the desorption system, namely: the time scale for atomic or wave packet motion on the potential curves in Fig. 2 and  $\tau_R$ , the resonance lifetime, both given in terms of  $\omega_0$ , the oscillator frequency of the well;  $D$ , the desorption energy; and  $\Delta z$ , the displacement of the minimum of  $V_-$  with respect to  $V_a$  which is a measure of the force on the adsorbate when it is a temporary negative ion. An example of the theoretical results [2] are shown as  $dN_{\text{des}}/dt$  vs.  $\omega_0\tau_R$  plots in Fig. 3 for a range of  $\Delta z$ , with  $D \approx 1$  eV (as for NO/Pt). An initial increase in desorp-



**Fig. 3.** Desorption rate versus resonance lifetime (in units of  $\omega_0 = 2\pi/T$  where  $T$ , the vibrational period associated with the adsorption potential well,  $\approx 70$  fs for NO/Pt) with selected values of displacement for  $V_-$ , the negative ion potential, with respect to  $V_a$ , as labeled. While the absolute scale of the  $dN_{\text{des}}/dt$  axis is arbitrary, the curves are properly scaled with respect to each other.

tion rate is experienced as  $\tau_R$  increases from zero due to the increasing displaced nuclear dynamics. Larger  $\Delta z$ , hence larger forces, results in larger desorption rates. Ultimately the diminishing electron capture rate implied by longer  $\tau_R$  wins out, the desorption rate achieves a maximum and then decreases with further increases in  $\tau_R$ . Emphasis has been placed on the crucial role of  $\tau_R$  because it is also the time interval between switching on and off the intermediate state potential. Human control of this attribute allows for the selective control of reaction outcomes [17], the hallmark of femtochemistry [2]. The unification of system characteristics of this sort has provided an intuitively clear picture of resonant hot electron induced bond excitation processes that has subsequently been used as the basic model in many new and developing areas of molecular processing in surface science, surface femtochemistry, current-driven STM atom transfer, manipulation, and fabrication, and in novel meso-scopic and nanotechnology applications.

Throughout the decade since this work was carried out, all five participants have remained active in various roles at NIST. The experimentalists continued their forefront studies in controlled, time-resolved molecular processes at surfaces, particularly those involving time-delay, pump-probe techniques to observe time-resolved phenomena at the femtosecond level. Some of this work has been summarized in a Feature Article in the *Journal of Physical Chemistry* [9]. The authors have presented numerous invited talks at international scientific meetings, workshops, and Gordon Conferences, introducing the surface science, chemical physics, and chemical

technology worlds to the allures and potentialities of surface femtochemistry. Lee Richter is currently developing new chemically sensitive probes for biologically interesting surfaces and interfacial systems based on near field scanning optical microscopy and on sum-frequency generation [18]. Steve Buntin is engaged in the study of radical reactions with well characterized surfaces that are of industrial relevance [19].

It appears that doing laser-excited surface experiments is good training for management careers at NIST. Over the intervening years, Rich Cavanagh has risen to become Chief of the Surface and Microanalysis Science Division. Buntin has succeeded him as leader of the Surface Dynamical Processes Group. Dave King spent five years as a program manager in the Advanced Technology Program and now serves as Science Advisor to the Undersecretary of Commerce for Technology. Bill Gadzuk has remained engaged in theoretical studies involving hot electrons, femtochemistry, tunneling phenomena [6], and related topics. In a recent commissioned Topical Review that appeared in the *Journal of Physics B* [20], he emphasized the intellectual stimulation provided by numerous NIST colleagues from other organizational units. As in many other NBS/NIST achievements, these cross-disciplinary interactions have played a key role in the success of his research. In at least one vision of an ideal world, this is how things should work!

*Prepared by J. W. Gadzuk.*

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