

## FEATURE ARTICLE

### Dynamics of Nonthermal Reactions: Femtosecond Surface Chemistry

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Optically driven surface reactions are attracting an increasing level of attention in the physical chemistry community. Not only have there been recent advances in establishing the viability of laser driven surface reactions, but there has also been an increased awareness of the need to understand the underlying reaction mechanisms. The necessity of accounting for energy-transfer processes that occur on the femtosecond time scale is now apparent. In this review the experimental and theoretical basis of our current understanding is surveyed, and prospective areas of advancement are considered.

#### I. Introduction

Molecular motion on the picosecond ( $10^{-12}$  s) and femtosecond ( $10^{-15}$  s) time scale is critical to chemical reactions. This fact has been established by many experimental findings, initially and still predominantly done in the gas phase (e.g., photodissociation line widths, reaction-product and beam-scattering distributions, chemical quenching rates, and pump/probe measurements), and by many theoretical results (e.g., the broad applicability of the RRKM approach, classical trajectory and wavepacket propagation studies of intramolecular vibrational relaxation, and simple  $A + BC \rightarrow AB + C$  reactions). One of the powerful tools in elucidating such ultrafast dynamics is laser radiation. Lasers can provide well-defined and well-controlled excitation to initiate a reaction and laser-based techniques permit the dynamics of the reaction to be examined in two complementary manners. First, sensitive laser spectroscopic measurements can provide a complete characterization of the reaction products, yielding their densities, velocities, and quantum-state distributions. Second, pulsed lasers afford the possibility of following, in real time, a rich spectrum of energy flow events including the transformation of reactants to products. With recent technological advances, chemical systems with spectral responses spread over a wide wavelength range can be studied with picosecond to femtosecond time resolution. These capabilities have led to a remarkable growth in laser-based studies of chemical dynamics.

Lasers have been widely exploited in elucidating picosecond and femtosecond dynamics in the fields of gas- and liquid-phase chemistry.<sup>1-3</sup> Application of laser probes of ultrafast dynamics has, however, been belated in the field of surface chemistry. This lag is certainly not due to a lack of relevant problems. Many major unresolved issues in surface dynamics concern phenomena occurring on the picosecond and femtosecond time scale. These questions relating to the ultrafast response and nonequilibrium behavior arise in the classical areas of surface science, such as catalysis and film growth, as well as in emerging technologies ranging from laser-driven processing in microelectronics<sup>4,5</sup> to solar energy conversion<sup>6</sup> and biotechnology.<sup>1</sup>

One may ask what has hindered the use of laser-based techniques to probe ultrafast dynamics at surfaces. The answer can be found in the complexity of the problems, both from the standpoint of experimental challenges and from the standpoint

of identifying well-defined optically activated processes. In regard to the former, the most informative experiments require state-of-the-art surface preparation facilities (frequently in ultrahigh vacuum) as well as state-of-the-art laser systems. As for the latter, candidate systems must not only have well-characterized initial states but must also exhibit reaction rates sufficiently high to compete with the rapid quenching generally found at surfaces.

Despite these challenges, the past few years have witnessed notable progress in the study of laser-driven processes at surfaces. In this article, recent advances in understanding the mechanisms involved in surface photochemical reactions and the associated ultrafast surface dynamics are reviewed. The different classes of optically excited surface reactions are defined and illustrated in section II. The paper is then organized around the two principal experimental approaches for such studies. In section III results concerning the final-state distributions for photochemical reaction products will be discussed. In these measurements, the reaction itself provides a clock and the ultrafast dynamics are revealed in the energy content of the products. In section IV direct time-domain studies of reactions and of energy relaxation are reviewed. In these investigations, a picosecond or femtosecond laser pulse suddenly produces a nonthermal distribution of energy in the surface, and the adlayer response that occurs as the perturbed system recovers to its equilibrium state is probed in real time with a second laser pulse. Both of these methods have provided significant new insight into the dynamics of chemical processes occurring on the picosecond and femtosecond time scale. Nonetheless, it will be seen that the optical excitation mechanisms and pathways for energy flow are much richer than those found in either gas- or solution-phase chemistry and that considerable work remains to be done to bring our understanding to the same level of sophistication as in these fields. Some of the future directions in the field are discussed in section V.

It should be noted that electron- and ion-induced surface processes generally involve nonequilibrium excitation and may, hence, share mechanistic features with photoinduced reactions.<sup>7-9</sup> Within the limited scope of this paper, no attempt will be made to address these processes in a systematic manner. We further restrict our attention to photoinduced effects involving low-energy (optical) photons and to processes involving solid surfaces. Finally, we wish to point out that many of the basic issues about rates and

modes of energy flow that arise in considering the ultrafast dynamics of photoinduced processes are also important factors in understanding the course of surface processes under equilibrium conditions. In this article, we emphasize the results related directly to the study of optically driven processes. Classical approaches, such as gas-surface scattering and spectroscopic measurements, have been reviewed elsewhere.<sup>10</sup>

**Background.** The allure of using lasers to optically stimulate surface chemistry has been with us for over 20 years.<sup>11,12</sup> and the number of systems where photoinduced surface reactions have been reported is rapidly growing.<sup>13-15</sup> Still, there is much that we do not understand about even the simplest optically driven reactions at surfaces. Elementary questions related to the nature of the initial excitation process remain to be answered. Issues that are just being addressed include those of how the radiation is absorbed by the system, how the energy reaches the surface, the extent to which the surface perturbs the excited state dynamics of the adsorbate, and how the energy of the reaction ultimately finds its way into the reaction channel.

Before we explore these areas of surface photochemistry and dynamics, a few comments on the impact of this active research area are in order. The ability to direct energy into specific bonds in order to activate a reaction has long been a major goal of laser chemistry. Similarly, the possibility of activating surface reactions, without activating bulk reactions, is key to many aspects of nanoscale chemistry. Surface reactions that are optically driven, that involve charge-transfer processes, and that incorporate chemical radicals are playing an increasingly important role in modern technologies. The underlying reactions often differ from those that can be achieved using other schemes and hence offer the potential for synthesis of surface layers with novel chemical and materials properties. To exploit these nonthermal reactions and to map out other optically accessible reaction channels, the operative excitation mechanisms and the time scales of the competing relaxation processes must be established.

A further important motivation for investigating the dynamics of optically induced processes at surfaces is the insight that such studies give into the course of purely thermal reactions. The coupling constants and rates of energy transfer, as fundamental properties of the system, are frequently important for a detailed understanding of thermally driven processes. For example, the sticking coefficient for a molecule approaching a surface at thermal velocities is determined by the dissipation of energy on the subpicosecond time scale of the collision of the molecule with the surface. The rate and nature of such energy flow is being elucidated in measurements involving optical excitations, such as the studies of vibrational relaxation and desorption induced by femtosecond laser pulses discussed below. It may be further remarked that because of the frequent occurrence of substantial activation barriers in surface processes, thermal reactions often require or produce species with substantial energies, on a scale comparable to that of visible photons.

Nonthermal reactions can be stimulated by optical excitation, as well as by means such as the bombardment of the surface by beams of electrons, ions, and radicals. The critical feature is that a non-Boltzmann energy distribution be achieved at the surface. Any reactions that occur before the incident energy has fully redistributed itself among all of the degrees of freedom of the system may show a distinctive nonthermal character. In the case of metal surfaces, where optically excited carriers typically equilibrate with the lattice temperature in a few picoseconds,<sup>16</sup> nonthermal channels can contribute only within the first several picoseconds following excitation. The time scale for optically excited carriers to reach electronic equilibrium is typically a fraction of a picosecond,<sup>17</sup> restricting even further the possibility for nonthermal reactions involving hot carriers. For semiconductors and insulators, the times for electronic excitations to equilibrate with the lattice and for carriers to achieve equilibration

amongst themselves will be different from those for metals. In each case, however, the accessible chemical reaction channels need not be restricted to those available to a thermally driven process, i.e., for a system where all the degrees of freedom can be described by a single temperature.

## II. Optical Excitation Mechanisms

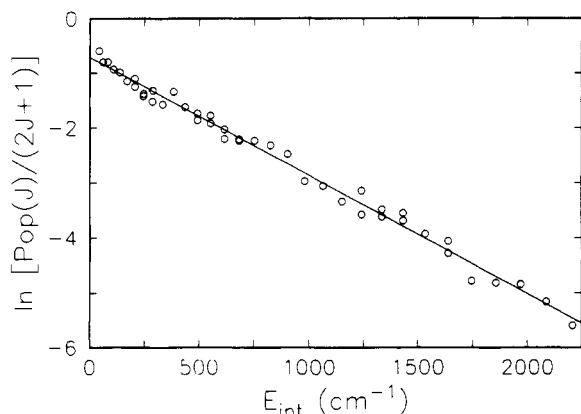
Coupling of optical photons into the surface layer can occur through four distinct mechanisms. The incident photon can directly excite an adsorbate-localized transition, it can excite a transition involving a surface-localized electronic state, it can create excited carriers in the substrate that subsequently couple to the adsorbate, or the optically generated carriers can degrade into heat that subsequently activates a reaction. The first three mechanisms can result in reactions that are best described as occurring on the ultrafast time scale. The final mechanism typically leads to the same products as would be observed using conventional heating techniques. However, the high heating rates obtainable with pulsed lasers may permit the observation of reaction channels, albeit thermally activated, that cannot be observed using standard heating processes.

**A. Thermally Driven Reactions.** The ability to optically activate conventional thermal chemical reactions is now well documented.<sup>18-24</sup> In a number of experiments, the ability of laser-surface heating to desorb molecular adsorbates has been exploited to follow various reaction processes. It has also been shown that the high heating rates available with pulsed lasers may alter the relative importance of certain reaction channels (those with large prefactors) with respect to conventional thermal chemistry. Since this literature has previously been reviewed,<sup>25</sup> no attempt will be made to cover this aspect of laser thermal desorption. However, four facets of thermally activated desorption are of particular interest for our purposes.

First, the validity of model calculations for laser surface heating of metals with pulses of nanosecond or longer duration has been experimentally confirmed.<sup>26-28</sup> These measurements established that the duration and magnitude of the rise in the near-surface temperature can, for typical experimental geometries, be accurately predicted by one-dimensional heat flow models.<sup>29</sup> As a result, calculations of the thermal evolution at a surface can be performed with confidence down to the nanosecond time regime.

Second, the pulsed laser heating of surfaces can be exploited in studies of surface diffusion of adsorbed species. Such measurements, giving insight into lateral barriers for motion and adsorbate-adsorbate interactions, are complementary to the desorption experiments discussed in detail in this paper. Measurements of the (chemical) diffusion rates are accomplished by producing an inhomogeneous surface density of the adsorbed species with a pulsed laser and then monitoring the subsequent return to the equilibrium structure. A simple and versatile approach consists of removing the adsorbed molecules under the laser spot by laser-induced thermal desorption and then monitoring the refilling of the depleted area with a subsequent laser pulse.<sup>30</sup> This method has been applied to determine diffusion of a variety of adsorbates on single-crystal metal surfaces. A recent further development in this area is the exploitation of adsorbate grating structures. By interfering two laser beams on the surface of the sample, it is possible to establish a periodically modulated temperature profile, which produces in turn a periodically modulated adsorbate density.<sup>31-34</sup> The relaxation of this type of density distribution can be followed by a measurement of the efficiency of light diffraction from this structure. The technique has been shown to permit the determination of a wide range of surface diffusion rates<sup>31,35,36</sup> and to be particularly well-suited for the characterization of anisotropic diffusion.<sup>37</sup>

Third, the energy content associated with the products of thermally activated surface reactions has been probed using state-



**Figure 1.** Rotational energy distribution of NO molecules desorbed from a Pd(111) surface using nanosecond laser-induced heating. The straight line is a fit to a thermal distribution corresponding to an rotational temperature of  $640 \pm 40$  K (after ref 20).

resolved diagnostics.<sup>38</sup> The final-state energy distributions reflect the nature and rate of energy flow in the transition state. In general the resulting distributions may differ appreciably from thermal distributions at the surface temperature. For the case of intact desorption of molecular species, the energy distributions of different degrees of freedom have typically been found to be nearly Boltzmann in character. The temperature describing these distributions may differ measurably from that of the surface. This effect is particularly pronounced using the high heating rates provided by laser excitation. The data in Figure 1 represent the rotational energy distribution for nitric oxide (NO) molecules thermally desorbed from a Pd(111) surface by a nanosecond laser pulse.<sup>20</sup> While the distribution is Boltzmann in character, it corresponds to  $T_{\text{rot}} = 640 \pm 40$  K for a surface temperature at the time of desorption of  $1100 \pm 100$  K. On the other hand, the vibrational energy distribution of the desorbed NO molecules was found to correspond to that expected for the surface temperature. Such energy distributions for thermally driven reactions provide an important point of comparison for the nonequilibrium processes described below. For these latter processes, much stronger departures from Boltzmann distributions are frequently observed.

Finally, optical excitations that result in surface reactions that are strictly thermally activated should not exhibit any dependence on the wavelength or polarization of the incident radiation, once the absorption properties of the substrate are taken into account. This independence of excitation wavelength and polarization may provide a simple test for photoreactions for which the thermal or nonthermal character is in doubt.

**B. Reactions Induced by Adsorbate-Localized Excitation.** Extensive effort has been exerted in the search for chemical events that could be attributed to adsorbate-localized excitation.<sup>39</sup> To understand the challenges associated with inducing photochemistry in adsorbed monolayers, it is instructive to consider the competitive deexcitation channels introduced by the presence of the substrate. An extremely valuable contribution to this area comes from the classical picture of an excited oscillator whose distance from the surface is treated parametrically.<sup>40</sup> This theory accounts for the coupling of excited states of adsorbates to the image field at distances as short as a few angstroms. However, at distances relevant to surface and interface chemical bonds, the validity of many of the assumptions in the theory begins to fail.<sup>41</sup> For instance, the assumption of a nonlocal potential becomes suspect, as does treatment of the adsorbate as a point dipole. Still, this elementary analysis reveals that rapid quenching of excitation is expected as molecules approach the surface. It further demonstrates the particularly high quenching efficiencies for metals and suggests the possibility of considerably weaker coupling of adsorbate electronic excitations to the surfaces of semiconductors and insulators.

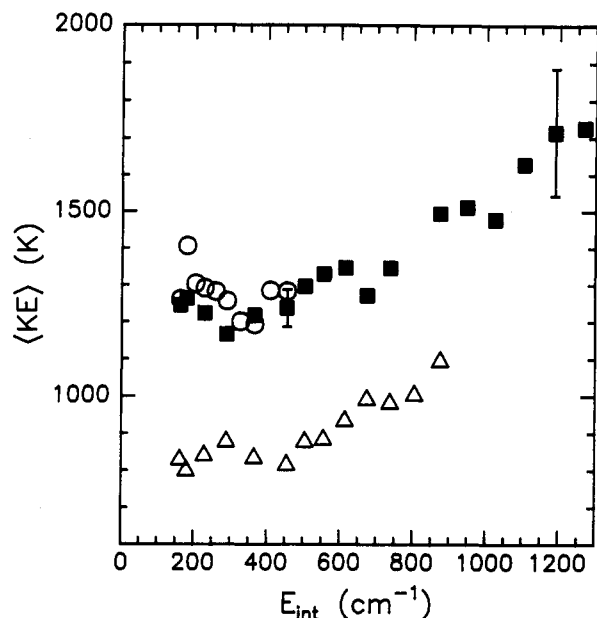
The systems where compelling evidence exists for adsorbate-localized excitations are limited to cases where the free adsorbate has a large cross section for photochemical processes. On metal surfaces, metal carbonyls have been reported to exhibit adsorbate-localized excitations by at least two groups.<sup>42,43</sup> Only a few further examples of adsorbate-localized photochemistry have appeared for metallic substrates.<sup>13,14</sup> As for semiconductor substrates, only the metal carbonyls have been reported to undergo adsorbate-localized photochemistry.<sup>44</sup> However, on insulators, in multilayers, or in physisorption systems, there are numerous citations of adsorbate-localized photoprocesses.<sup>45–50</sup> In these cases, the weak coupling to the substrate has two significant implications for surface photochemical processes. It essentially eliminates all substrate mediated relaxation processes other than those predicted by classical coupling theories and multiphonon decay. In addition, it suggests that the mechanisms of the resultant surface photochemistry will not substantially differ from those achieved with a clean surface that interacts with either gas- or condensed-phase photolysis products.

**C. Carrier-Induced Reactions.** When an adsorbate-covered surface is exposed to optical radiation, only a small fraction of the light can be adsorbed by a single monolayer. Consequently, unless the substrate is almost entirely transparent, more energy will be deposited in the underlying solid than in the adsorbate layer. For optical radiation in the near-infrared and shorter wavelength regions, the photons are generally absorbed by the creation of carriers, i.e., through the production of electron-hole pairs in the solid. As has now been clearly demonstrated experimentally, these carriers may lead to nonthermal surface reactions.

Let us first consider the fate of electron-hole pairs after their production. Initially these carriers are far out of equilibrium with the temperature of the substrate. They can undergo collisions both with other carriers and with phonons. The time over which the carriers retain excess kinetic energy depends on the features of the material system, as well as on the optically produced carrier density.<sup>17,51</sup> Typically these hot carrier lifetimes lie in the range of  $10^{-10}$ – $10^{-9}$  s. When the carrier density is sufficiently high, the carriers may equilibrate among themselves to establish an effective electronic temperature greater than that of the lattice. This electronic temperature will typically decay to the lattice temperature on the time scale of 1 ps.<sup>16,52</sup> In metals, the carriers relax directly to thermal equilibrium with the lattice. In the case of insulators or semiconductors, in which bandgaps exist, the electrons will initially cool to the bottom of the conduction band and the holes will cool to the top of the valence band. The lifetime of the thermalized excitation will be controlled by the available decay channels, which include diffusion away from the surface, surface mediated recombination, and radiative recombination. The resulting lifetimes vary widely but may extend into the nanosecond range and beyond.

For the case of metals, the lifetime of nonequilibrated electronic excitation is always short. From this fact, it was widely inferred in the past that photochemistry would be strongly suppressed or nonexistent. As it has been revealed experimentally, however, metal substrates are capable of supporting nonthermal reactions, either from the adsorbate-localized excitations discussed above or from carrier-mediated processes.<sup>19,53–59</sup> That bulk carriers should indeed initiate reactions can be understood when it is realized that the mean free path of an excited carrier is generally comparable to the 10–20-nm penetration depth of the optical radiation in a metal. Thus each absorbed photon is in fact likely to produce a hot carrier impinging on the surface, which may in turn induce a nonthermal reaction.

Such a carrier-mediated process is illustrated nicely in studies of NO/Pt(111). In this system, the nonthermal nature of the desorption process is reflected in the high kinetic energy measured for the desorbed NO molecules compared with the modest jump

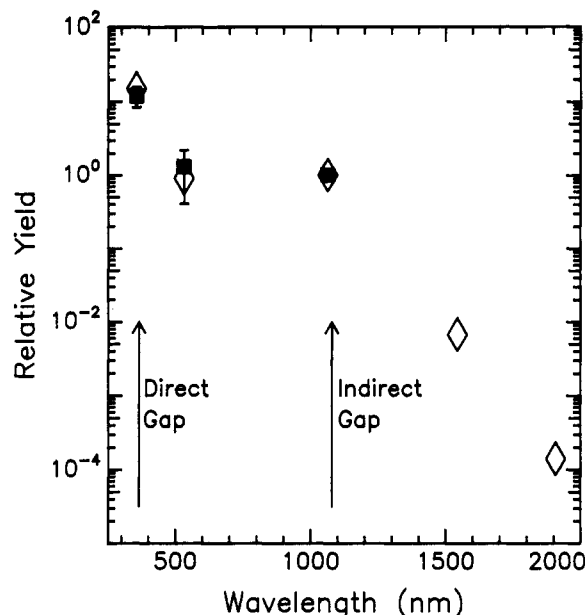


**Figure 2.** Mean kinetic energy as a function of internal energy for NO desorbed from Pt(111). Results for calculated peak surface temperatures of 300 K for three different desorption laser wavelengths are shown as ( $\Delta$ ) 154 nm, ( $\blacksquare$ ) 532 nm, and ( $\circ$ ) 355 nm (after ref 19).

( $\leq 100$  K) in the equilibrium lattice temperature associated with the laser radiation.<sup>19,53</sup> Figure 2 displays the dependence of the kinetic energy of desorbed NO (in states of varying internal excitation) on wavelength observed for the NO/Pt(111) system.<sup>60</sup> Given that the kinetic energy was independent of pulse energy (with the desorption yield increasing linearly with pulse energy), that the mean kinetic energy depended on internal state, and that the kinetic energy showed a clear dependence on incident wavelength, thermally activated channels can be dismissed in favor of a desorption mechanism driven by excited carriers. In view of the brief lifetime of excited carriers and the strong coupling of excited states at metal surfaces, it follows that the relevant excited-state lifetimes in this nonthermal process are in the femtosecond regime.

The behavior for NO/Pt(111) can be contrasted with the results mentioned earlier for the similar system of NO/Pd(111).<sup>20</sup> Although excitation by nanosecond laser pulses was employed in both of these studies, the regime probed for NO/Pd(111) was one of considerably greater laser fluence. The higher laser fluence produced a sufficient temperature rise to allow thermal effects to completely dominate any photochemical processes. The thermal and nonthermal desorption mechanisms could be differentiated by the character of their final-state distributions, as well as the differing dependencies of the two processes on the fluence and wavelength of the laser excitation. A further point of comparison is the behavior observed for the NO/Pd(111) system when excited by laser pulses of only 200-fs duration.<sup>57</sup> In this case, the desorption process is clearly incompatible with a conventional thermal desorption mechanism based on the equilibrium temperature rise of the substrate, as manifest in both the high desorption yield and the energy distributions of the desorbed molecules. The distinctive aspects of the desorption process in this regime arise from the capability of attaining very high densities of electronic excitation in the substrate from the subpicosecond laser pulse. A more complete treatment of these and related experiments is given in section IV.A.

At approximately the same time as the NO/Pt(111) experiments were reported, a series of papers appeared that focused on the surface photochemistry of methyl halides physisorbed on metals. Several desorption channels were identified, ranging from direct photofragmentation of the methyl halide to electron attachment by the methyl halide of photoelectrons generated in the substrate.<sup>61,62</sup> While the photofragmentation channel was



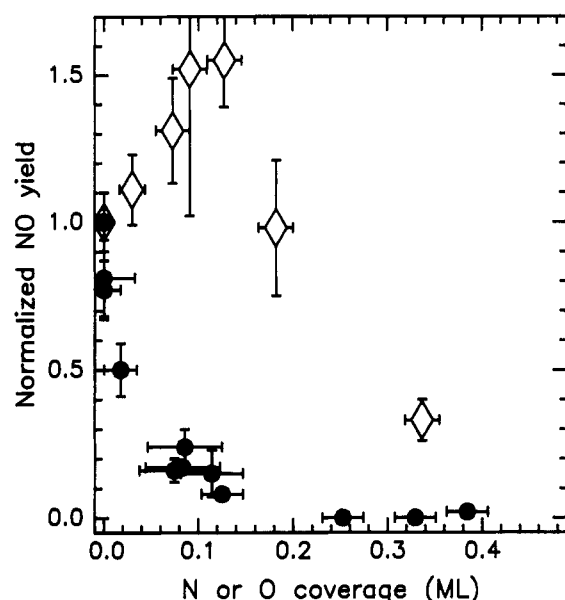
**Figure 3.** Wavelength dependence of the photodesorption yield of NO from Si(111)  $7 \times 7$ . Data for ( $\diamond$ ) p-type and ( $\blacksquare$ ) n-type substrates are normalized at 1064 nm. The direct and indirect gaps of Si are indicated (after ref 66).

found over a large coverage range ( $\theta \geq 1$ ), the electron attachment channel was only observed near monolayer coverages. A model was developed attributing a 15-fs time scale to the excited state accessed by the photoattachment process.

In all of the cited experiments,<sup>53-55,58,61,62</sup> the role of the substrate in altering the excited-state properties of the adsorbed molecule is clear. In each case, substrate-localized levels participate in the photoinduced reaction. Either they supply excited carriers to the adsorbate or they provide a sink where the adsorbate releases its excess energy. Thus, the surface photochemistry is dramatically altered from the photochemistry that would be anticipated for the same adsorbate molecule in a gas-phase environment.

**D. Surface-State-Mediated Reactions.** The fourth mechanism for optically exciting surface chemistry, that relying on electronic transitions associated with the surface of the solid, is perhaps the most complex mechanism and the one in which the role of the surface is most distinctive. The optical transition in this case involves at least one state (either occupied or unoccupied) that is localized in the surface region. While an adsorbate-localized transition would fit this definition, here we wish to draw attention to the effect of the delocalized states of the surface. Due to the asymmetry of the vacuum-solid interface, new electronic states that deviate from those of the underlying bulk are expected on clean surfaces. The photoemission literature contains numerous elegant examples of these new surface states.<sup>63,64</sup> (In general, a distinction is made between surface states and surface resonances,<sup>65</sup> but the two will be treated on equal footing for the purposes of this article.) The same lifetime arguments that were given in the case of adsorbate-localized excitations still apply to these electronic states. However, surface states may offer an additional selectivity for optically induced chemistry at surfaces, as adsorbates not bound to sites with the correct surface-state electronic structure will not be activated.

Surfaces of semiconductors provide a clear example of the influence of surface states in optically driven reactions. For single-photon processes, the bond energy dictates the minimum photon energy capable of initiating a specific reaction. If radiation below the bandgap of the substrate is found to be capable of supplying this minimum energy, then the ability of subbandgap radiation to induce reactions can be explained only by adsorbate-localized or surface-state mediated events. A compelling example of this effect comes from the NO/Si(111)  $7 \times 7$  system.<sup>66</sup> Figure 3



**Figure 4.** Desorption yield for NO from Si(111) when coadsorbed with (●) NH<sub>3</sub> and (◇) O<sub>2</sub> as a function of coadsorbate coverage (after ref 66).

shows the dependence of the NO desorption yield as a function of excitation wavelength. Note that there is a substantial yield even when the energy of the photolysis photon falls below that of the (indirect) bandgap. This observation clearly rules out bulk carriers as the driving force for desorption in this system, as no bulk carriers are generated with subbandgap radiation. In addition, Figure 4 shows the influence of two different coadsorbates on the NO photodesorption yield. From photoemission studies it is known that each of the coadsorbates in the low exposure limit interacts selectively with different surface electronic states: NH<sub>3</sub> affects the rest-atom-localized S<sub>2</sub> state and O<sub>2</sub> affects the adatom-localized S<sub>1</sub> state.<sup>67</sup> The prompt quenching of NO photodesorption observed in the case of coadsorbed NH<sub>3</sub> and the delayed onset of quenching in the case of O<sub>2</sub> suggest that the S<sub>2</sub> surface state mediates the photodesorption of NO. The model for the photodesorption of low coverage NO/Si(111) 7 × 7 that emerges from this work is as follows. An optically generated hole is trapped in the rest-atom-localized S<sub>2</sub> state; this excitation couples to the adatom-bound NO, resulting in prompt desorption.<sup>66</sup> At NO coverages approaching saturation, the 7 × 7 reconstruction is lifted, the surface states are removed, and the energy distribution of the desorbed NO is dramatically altered.<sup>68</sup> The potential for exploiting surface electronic states to drive photoreactions at selected surface binding sites merits further attention.

**E. Synopsis.** As the brief survey above illustrates, photochemistry on surfaces has now been observed experimentally in many different systems. The mechanisms by which photochemical reactions occur are diverse. In addition to the possibility of light simply inducing thermal chemistry, true photochemical processes may occur through several mechanisms involving localized excitation of the adsorbate or surface states, as well as through processes mediated by bulk carriers. From the experimental point of view, nonthermal chemistry can generally be identified by features of the reaction products. In particular, product yields will generally scale linearly with laser fluence and nonthermal final-state energy distributions will be observed.

Distinguishing between different mechanisms for photochemical processes is frequently more difficult. The nature and energy distribution of the products is one of the key ingredients in developing a complete picture of the reaction pathways, just as for gas-phase processes. This point will be examined in detail in the next section. As will be seen in section IV, ultrafast measurements have also now been developed as powerful tools for elucidating coupling strengths and reaction mechanisms.

Finally, we should emphasize that the wavelength dependence of the process may be quite useful in identifying the nature of the reaction mechanism. For carrier-driven processes, for example, it is often possible to distinguish between bulk carrier effects and surface-state effects based on the wavelength dependence of the photoresponse. Similarly, in adsorbate-localized photochemistry, resonances associated with the optical absorption spectrum of the adsorbate may provide a valuable indication of the excitation mechanism. Under favorable circumstances, additional insight into the nature of photochemical mechanisms at surfaces can also be obtained from studies of the sensitivity to angle of incidence and polarization of the incident laser beam.<sup>69</sup> While characterization of the spectral response alone may not always lead to an unambiguous identification of the pathway for activating the chemical process, it can frequently eliminate one or more candidate reaction channels.

### III. Ultrafast Dynamics Probed through Final-State Distributions

The cases identified in the preceding section are indicative of the broad range of laser-driven surface processes which, on the femtosecond time scale, could exhibit unusual chemical manifestations. Each mechanism provides a different coupling of the adsorbed surface molecules to an excited electronic state (or short-lived intermediate) that is critical for the ensuing chemical reaction. In this section we consider a variety of problems where an initial laser excites the surface, and a second laser provides a probe of the photodesorbed molecules. It should be noted, however, that the dynamics of steady state surface processes, ranging from recombinative desorption to adlayer oxidation, can also benefit from application of these state-resolved techniques. In the interest of brevity, the following discussion is restricted to photostimulated processes.

**A. Dynamics of Photodesorption: Experimental Techniques.** As indicated above, characterization of the energy partitioning in the gas-phase products following optical irradiation of a surface can provide a great deal of information on the nature of the excited states and energy transfer mechanisms involved in the reaction. The most detailed measurements of energy partitioning come from state-specific detection techniques such as laser-induced fluorescence (LIF) or resonance enhanced multiphoton ionization (REMPI). This state-resolved approach has been applied widely to NO and to a limited number of other systems with varying degrees of state specificity.<sup>15</sup>

The final-state distributions, which include kinetic-energy, angular, and quantum-state distributions, often display several distinctive attributes for photodesorption processes. Here we briefly discuss some of the common trends. First, we would like to comment on the remarkably strong dependence of photodesorption processes on the detailed initial condition of the system. Consider, for example, the influence of the surface coverage of the adsorbate. For both the systems of NO/Pt(111) and NO/Si(111), strong coverage effects are present.<sup>19,53,66,68</sup> In the case of Pt(111), no photodesorption could be observed for NO coverages  $\theta \leq 0.25$  ML (ML = monolayer) while additional desorption channels were evident for  $\theta_{\text{NO}} \geq 0.5$  ML. For the Si(111) surface, all aspects of the desorption dynamics change as the NO coverage increases from 0.03 ML to saturation. Although the substrate temperature,  $T_s$ , determines those binding sites that will be occupied, there is an additional influence of  $T_s$  on energy distributions in the desorbed species. In the few cases where careful temperature dependencies have been obtained,<sup>19</sup> it has been found that the kinetic energy and internal state populations show an approximately linear dependence on  $T_s$ . This implies that motion on the ground-state potential energy surface can also influence the final-state energy distributions.

A second general feature for photodriven processes is the nonthermal energy distributions of the products. One distinctive



aspect of such nonthermal distributions is the common occurrence of a positive correlation between the mean kinetic energy and rotational energy of the desorbed species, as we have already seen for NO/Pt(111) in Figure 2. In addition to this example of a hot carrier-driven process from a metal surface,<sup>19,70</sup> surface-state-mediated processes in semiconductors (NO/Si at low coverage),<sup>66</sup> bulk-carrier-induced processes on semiconductors (NO/Si at high coverage),<sup>68</sup> and charge-transfer processes on oxides (NO/NiO),<sup>54</sup> all exhibit the same behavior. This tendency toward higher kinetic energy with increasing rotational energy remains to be fully explained. One possible line of reasoning attributes the correlation to the greater phase space available for translational motion for high rotational quantum numbers. This behavior would be expected if the translational and rotational densities-of-states show the same functional dependence on total energy.<sup>71</sup> A second explanation can be formulated provided that the equilibrium orientation of the adsorbate in the excited state differs significantly from that in the ground state. Then both the translational and rotational energy of a molecule will increase together as the molecule moves on the excited-state potential surface.<sup>72</sup>

Angular distributions strongly peaked about the surface normal represent a third common trait of photodesorption. In contrast, angular distributions similar to  $\cos \theta$  observed in beam-surface scattering experiments for trapping-desorption channels have been taken as an indication that the scattered molecules achieve some level of equilibration with the surface. Apparently, the photodesorption processes are sufficiently prompt that the ejected fragments have not had sufficient time to reach a comparable degree of equilibration with the solid. Quantitative laboratory characterization of the angular distributions of these processes is becoming more routine.<sup>73-75</sup> The motivation behind determining the angular distributions lies in their correlation with the corrugation of the potential energy surfaces involved in the desorption process. Such studies may also be useful in elucidating adsorbate structure and orientation in the ground state, as in the technique of ESDIAD (electron-stimulated desorption ion angular distribution)<sup>76</sup> for excitation by electron beams.

While the preceding discussion would seem to suggest that very similar potential energy surfaces may be involved for these various desorption systems, a much different picture emerges if one examines the population of the spin-orbit or vibrational levels of the NO molecules desorbed from metal and semiconductor surfaces. For the hot carrier initiated desorption of NO from Pt(111), there is a marked inversion in the spin-orbit population, for NO from low coverage NO/Si(111) there is a strong propensity to form NO in the ground spin-orbit state, while for saturation coverage NO/Si(111) the spin-orbit population is completely equilibrated with the Boltzmann-like rotational distribution. These effects in the spin-orbit populations are illustrated in Figure 5. The  $v = 1/v = 0$  ratio of vibrational populations of NO molecules desorbed from Pt(111), Si(111) at low coverage, and Si(111) at high coverage were reported to be 0.04, 0.19, and 0.54, respectively.<sup>53,66,68</sup> Some of this variation is expected when comparing metallic to semiconducting substrates, since the excited-state lifetimes could be vastly different. Yet these differences probably represent major variations in the contours of the potential energy surfaces traversed during desorption. Hence, despite the remarkable similarities between the kinetic energy distributions and the angular distributions, it is clear that an accurate description of photodriven processes will require a set of potential energy surfaces and energy-transfer rates reflecting the detailed characteristics of the system under study. Further, we see that interpretation of a particular aspect of the energy distribution of the desorbed fragment remains problematic without the benefit of a more encompassing knowledge of the final-state population distribution.

**B. Dynamics of Photodesorption: Theory.** Theoretical models capable of providing a detailed account of the experimental results

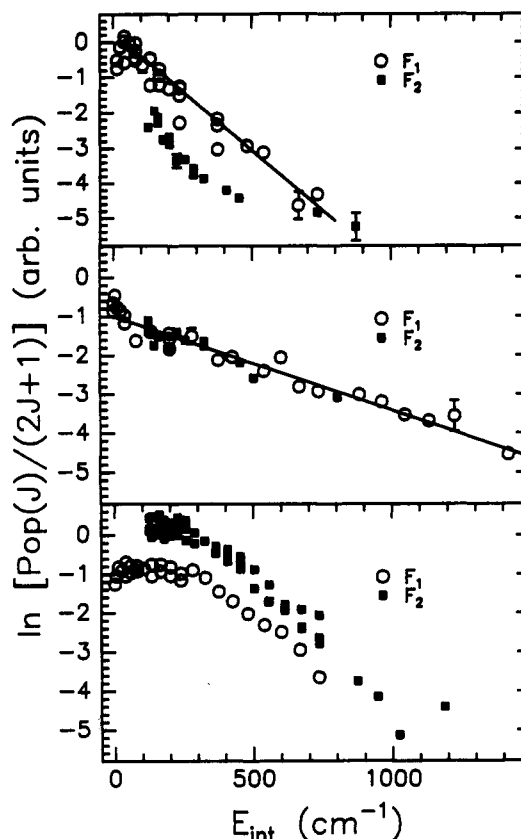


Figure 5. Internal energy distributions for NO desorbed from three different surfaces: (top) low coverage NO on Si(111) where surface states mediate photodesorption; (middle) NO-saturated Si(111) where the surface states have been removed; (bottom)  $\theta_{\text{NO}} = 0.5$  ML on Pt(111) where desorption is attributed to hot electron effects (after refs 19, 66, and 68).

that emerge from these state-resolved measurements are still being developed. To date, interpretation must rely primarily on a combination of heuristic arguments and explicit calculations of the dynamics for simple potential energy surfaces. The present approaches generally suffer from a lack of quantitative information regarding potential surfaces, particularly with respect to the excited-state surfaces. However, valuable guidance as to the qualitative nature of the interactions that contribute to these nonthermal processes has emerged from existing models. In the case of adsorbate-localized excitations, arguments based on the vibrational period of the  $\text{CH}_3\text{-Cl}$  bond led to an estimate of 15 fs for the photolytic bond breaking in the  $\text{CH}_3\text{Cl/Ni}$  system.<sup>62</sup> In the case of  $\text{Fe}(\text{CO})_5/\text{Ag}(110)$ , comparison of the photolysis quantum yield to the expected classical<sup>40</sup> image dipole damping time was used to estimate that the Fe-CO bond must be ruptured within 0.3 ps after excitation of the adsorbate.<sup>42</sup>

To predict the final-state energy distribution for photoinduced processes in a more quantitative manner, calculations involving motion on the appropriate potential energy surfaces must be introduced. These are calculations of desorption induced by electronic transitions (DIET). Such processes may follow the scheme embodied in the Menzel-Gomer-Redhead (MGR) model<sup>77,78</sup> originally introduced to describe electron stimulated desorption. In this picture, the adsorbate makes a Franck-Condon transition to a repulsive potential energy surface by a transfer of charge. If the adsorbate remains on this potential surface for a sufficient period of time, it may gain enough energy to desorb upon deactivation to the electronic ground state. A variant of this model proposed by Antoniewicz<sup>79</sup> is one in which the excited-state surface corresponds to a bound state and is attractive in the Franck-Condon region of interest. Motion on such a potential may also allow the adsorbate to escape from the potential well upon deactivation. For either type of excited potential energy

surface, it can be seen that measurable desorption may occur for excited-state lifetimes down to several femtoseconds, consistent with the observed nonequilibrium energy of the desorbed molecules.

While the qualitative features can be understood from approximate potentials, experimental observations such as those reviewed above indicate that even relatively subtle changes in the topology of the potential energy surfaces may exert a distinct influence on the final population distributions. One approach to testing the general validity of different potential energy surfaces has been to follow the trajectories on idealized excited-state potential energy surfaces. Both classical trajectory studies<sup>72</sup> and the propagation of wavepackets<sup>80,81</sup> on candidate potential energy surfaces have been explored. These efforts have established conditions where the resultant energy distributions are consistent with the experimentally observed distributions. These approaches have been successful in explaining not only the desorption yield but also the degree of vibrational excitation in the desorbed molecules.<sup>80</sup> However, the calculations to date are sensitive only to the magnitude of the curvature in the excited state and not to its sign. Consequently, it has not been possible to more firmly establish many details of the excited states involved, such as the attractive or repulsive nature of the excited state potential.

The need for realistic ground- and excited-state potentials will continue to be an important issue. Some progress is being made in this area. Through an insightful application of *ab initio* density functional techniques to calculate the potential energy surfaces relevant to neutral and ionic (both positive and negative) adsorbates, a clearer picture of nonthermal desorption has started to emerge for model systems.<sup>82</sup> The underlying interactions of the excited-state surfaces can be seen in the calculations for fluorine atoms and ions interacting with a jellium substrate. In this case, the degree of charge delocalization due to the presence of excited states (either  $F^-$  or  $F^+$ ) was clearly demonstrated. These calculations also revealed that intuitive pictures of the extent of charge transfer can be highly misleading, since the interaction with the positive fluorine ion was purely repulsive, but the negative ion showed a transition region from attractive to repulsive. While a full unit of charge may not be transferred in the majority of nonthermal surface processes, the trends and general expectations that have emerged from these calculations provide a valuable basis for understanding many aspects of carrier mediated reactions. As nonthermal reactions are probed in greater detail, it will become increasingly important to establish more clearly the characteristics of the potential surfaces involved.

#### IV. Ultrafast Dynamics Probed in the Time Domain

While analysis of the energy distribution in the final products of laser-induced surface reactions can be quite informative, there are questions related to the behavior of the adsorbed layer that cannot be addressed using techniques that only sample the desorbed species. In most of the photostimulated desorption processes that have appeared in the literature, the major fraction of the incident energy is partitioned to the solid and does not emerge in the desorbed species. The gas-phase detection techniques highlighted in the previous section provide only a limited capacity to track the partitioning of energy within the solid. Moreover, for the large class of surface reactions that do not lead to gas-phase products, measurements based on the detection of desorbed species are powerless. To clarify the evolution of the adsorbate as it is transformed from a stable reactant to a stable product, techniques are required that can monitor the adlayer during the course of the transformation. Picosecond and femtosecond probes that monitor directly the excited surface hold promise for addressing the evolution of the optically excited adlayer as it reacts or returns to its equilibrium configuration. Recently several time-resolved methods have emerged that are capable of characterizing surface layers on the

femtosecond time scale, including second harmonic generation (SHG),<sup>83</sup> sum-frequency generation (SFG),<sup>84</sup> laser-driven photoemission,<sup>85</sup> time-resolved infrared reflection-absorption spectroscopy (IRRAS),<sup>86</sup> and time-resolved reflection high-energy electron diffraction (RHEED).<sup>87</sup> These ultrafast laser probes are beginning to reveal the nature of the transient excited adlayers that are generated during laser-induced surface reactions.

**A. Dynamics in the Surface Layer: Experimental Techniques.** *Melting.* Laser-induced melting is a near-surface bulk effect that has been the subject of considerable scientific and technological interest. While there now exists convincing evidence that the process can be described by a conventional thermal model down to the subnanosecond time scale,<sup>88</sup> the behavior in the pico- to femtosecond regime has been scrutinized only recently. In this regime, it is possible to produce a high transient density of electronic excitation without a corresponding heating of the lattice. Thus the question arises whether this dense electronic excitation may induce disordering of the lattice without going through the usual step of heating the lattice. Such a scheme of "electronic disordering" was first proposed a number of years ago<sup>89</sup> but could never be substantiated with nanosecond excitation pulses.

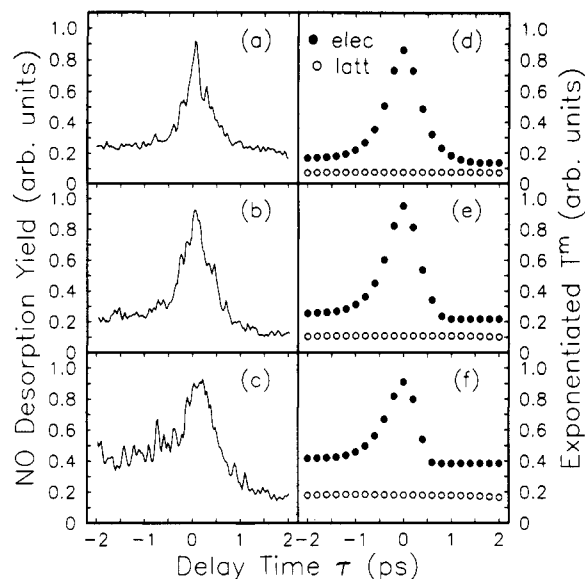
To examine these processes on the ultrafast time scale, one generally utilizes a pump-probe scheme in which a first intense laser pulse initiates the phase transformation and a second weaker pulse, introduced at a controlled delay time, serves as a monitor. For this purpose, both linear reflectivity<sup>90,91</sup> and second-harmonic generation<sup>83,92-95</sup> have been employed as probes. In the case of cubic materials, the second-harmonic measurement, which relies on a third-rank anisotropic tensor element (present for a material with cubic symmetry but lacking for a disordered medium<sup>96</sup>), provides additional information about the crystal symmetry that is lacking in the linear reflectivity signal. The anisotropic component of the SHG response provides a natural mechanism for monitoring the loss of crystalline order. It must, however, be noted that such optical probes do not give direct structural information. The structure of the material is felt only through its influence on the electronic properties. Thus careful interpretation of purely optical measurements is essential.

Time-resolved SHG has been applied to transient melting of both  $Si$ <sup>83,92</sup> and  $GaAs$ <sup>93-95</sup> surfaces. In these studies it was found that the anisotropic response of the signal may disappear in times as short as 100 fs. These observations, taken together with the sharp threshold in laser fluence in the transient signals, are difficult to reconcile with a conventional thermal melting mechanism. The measurements provide evidence for the intriguing possibility of driving a phase transformation in the surface layers of a solid by a strictly electronic process.

Complementary to these purely optical measurements are those in which a conventional probe of structure, such as X-ray or electron diffraction, is employed in a time-resolved mode. Considerable progress is currently being made on improving the time resolution of these techniques through the use of laser pulses to trigger the probe beam. Such a laser-driven pulsed electron beam has, for example, permitted Elsayed-Ali and co-workers to perform diffraction measurements with a time resolution of a fraction of a nanosecond.<sup>87</sup> This approach has been recently applied to an elegant study of the dynamics of surface disordering of  $Pb(110)$  using RHEED.<sup>97</sup>

*Desorption.* As the discussion of section III illustrates, final-state distributions for laser-induced processes can yield important information about energy transfer and reaction pathways. Real-time measurements of these processes provide a critical complement to these investigations. Recent experimental studies have demonstrated the possibility of following the simplest surface reaction of desorption with subpicosecond time resolution.

In work at IBM, it was shown that visible laser pulses as short as 200 fs in duration could be utilized to desorb molecules in a highly controlled fashion. These studies were carried out for NO



**Figure 6.** Correlation traces for the total desorption yield of NO/Pd(111) under excitation by a pair of femtosecond laser pulses as function of temporal separation between the pulses. The experimental data are shown in (a–c) and the corresponding exponentiated peak temperatures for the lattice and electron baths obtained from calculations are depicted in (d–f). (a) and (d) represent excitation pulses of equal energies, (b) and (e) excitation pulses of slightly different energies, and (c) and (f) pulses of appreciably different energies. Negative delay times indicate that the weak pulse precedes the stronger one (after ref 57).

molecules chemisorbed on a Pd(111) surface, a system that has been thoroughly characterized by means of the traditional tools of surface science and for which final-state distributions have been measured for thermal desorption by nanosecond laser pulses (section IIA).<sup>20</sup> It was found that at fluences well below the damage threshold, a 200-fs laser pulse desorb in excess of  $10^{-3}$  ML of NO molecules. Thus, a complete analysis of the final-state distributions for desorbed molecules could be obtained for femtosecond excitation.<sup>56</sup> The study revealed several remarkable features. The desorption yield was found to be strongly nonlinear in laser fluence. This behavior differs dramatically from that observed for photodesorption of NO/Pt(111) and NO/Si(111) by nanosecond laser pulses discussed in section III. On the other hand, experimental results such as the large desorption yield and elevated vibrational excitation of the desorbed NO molecules ( $T_v > 2000$  K) could not be understood in terms of a conventional thermal desorption mechanism. It was concluded that desorption is induced by the high density of electronic excitation, i.e., by the transient rise in electronic temperature. Indeed, modeling of the response of the metal using a coupled diffusion equation for the electronic and lattice excitations predicted electronic temperature transients of  $\sim 3000$  K.

In a subsequent set of experiments,<sup>57,98</sup> the IBM group introduced a correlation scheme to provide direct time-domain information about the desorption process. This method involved recording the time-integrated desorption yield when the sample was irradiated by a pair of excitation pulses introduced at a controlled temporal separation. A correlation response from the system was anticipated because of the nonlinear dependence of the desorption yield on laser fluence. Figure 6a shows results obtained when the sample is exposed to a pair of 400-fs excitation pulses of equal strength. A correlation feature results with a width of 600 fs (fwhm). This very fast response immediately rules out a desorption process driven by lattice excitation, since the characteristic time constant for relaxation of lattice excitation lies in the range 10–100 ps. The contrast between a mechanism driven by lattice excitation and electronic excitation is exemplified by the phenomenological modeling of Figure 6d. Here two limiting cases are considered. The desorption rate is assumed to be governed by the Arrhenius expression appropriate for thermal

desorption under conventional conditions but evaluated using either the lattice or the electronic temperature profile. Clearly a mechanism involving electronic excitation must be responsible for the desorption process. Figure 6b,c show experimental data for excitation by pairs of pulses of differing strength. The noticeable asymmetry of the correlation function is indicative of a finite response time of the system.<sup>57</sup> Both the presence of this asymmetry and its characteristic shape is reproduced by the model based on the electronic temperature transient (Figure 6e,f). An instantaneous mechanism such as a multiphoton process in the adsorbate would not be consistent with these experimental findings. Ultrafast correlation features have recently been observed for the desorption of O<sub>2</sub> from Pd(111)<sup>99</sup> and Pt(111)<sup>100</sup> surfaces.

An alternative experimental approach involves time-resolved second harmonic generation to follow the desorption process.<sup>101,102</sup> This approach was first applied on the subpicosecond timescale by Prybyla et al.<sup>102</sup> at AT&T Bell Laboratories. The information obtained from such a measurement is related to, but distinct from, that given in a correlation measurement. At the simplest level of interpretation, the SHG measurement reveals how long the adsorbate molecules remain on the surface, while the correlation width yields the lifetime of the excitation responsible for desorption. In the work of Prybyla et al., the system of CO/Cu(111) was examined using excitation with visible laser pulses of 100-fs duration. The SHG probe displayed an extremely rapid transition to its final value characteristic of a surface with a reduced adsorbate coverage. From these observations it was concluded that the CO molecules are desorbed within a period of roughly 300 fs. Again in these investigations a strongly nonlinear dependence of the desorption yield on laser fluence was observed. From the combination of this finding and the extremely short duration of the desorption process, it was concluded that the process could not be described either by a conventional thermal or photochemical mechanism. The elevated electronic temperature was identified as the driving force for desorption and a multiple electronic excitation mechanism was proposed to account for the strong coupling of the center-of-mass motion of the adsorbate and the substrate electronic excitation.

The detailed microscopic mechanisms that may be responsible for the desorption under these conditions of high electronic excitation densities are discussed later in this section. What is immediately clear from the experimental findings is that the center-of-mass motion of the adsorbate is controlled by electronic excitation and that the response occurs on a subpicosecond time scale. It should be noted that these studies relate both to the photoinduced processes discussed in section III (which occur in the limit of a low density of electronic excitation) and to vibrational relaxation measurements (which probe coupling of adsorbate vibrations to the substrate in a regime of modest perturbations from equilibrium) reviewed below.

**Adsorbate Vibrational Dynamics.** The ability to monitor vibrational excitation with high temporal resolution on surfaces has now been demonstrated by both conventional infrared spectroscopy carried out with pulsed laser radiation and with the technique of infrared-visible sum-frequency generation. These methods offer the capability of monitoring surface dynamics in an adsorbate-specific manner. As such, they hold the potential for following surface chemical reactions on a time scale limited only by the duration of the laser excitation pulse. Further, these techniques are extremely powerful methods for elucidating the nature and dynamics of vibrational excitations of adsorbed species. Clearly this basic information is central to developing a complete picture of the course of surface chemical processes. In this subsection, we present a brief overview of this very active area of research. We first discuss the direct time-domain determination of the lifetimes of vibrational excitations on surfaces, concentrating on surfaces where the initial excitation decays through the creation



of multiple lower frequency vibrations in the system. We then turn our attention to surfaces where the excited vibrations decay through resonant coupling to the electronic excitations of the substrate. These measurements also provide new insights not only into the rate of energy flow between the adsorbate and the substrate but also, as we remark next, into the adsorbate-adsorbate coupling strengths and the nature of higher lying vibrational states of the adsorbate layer.

**Multiphonon Damping.** The first quantity to consider in describing the dynamics of vibrational excitation in adsorbates is the excited-state population decay time,  $T_1$ . Such vibrational lifetimes have been measured rather extensively on the surfaces of high-area systems.<sup>86,103-105</sup> Vibrational lifetimes for the high-frequency OH and OD stretching modes on SiO<sub>2</sub> particles were determined to be  $220 \pm 20$  and  $135 \pm 10$  ps, respectively, times that are relatively slow as they correspond to  $10^4$  vibrational periods. From the strong temperature dependence measured for  $T_1$ , it was proposed that the relaxation was controlled by multiphonon decay pathways. By comparison to the decay rates observed for silanol (R<sub>3</sub>SiOH) molecules in solution, it was concluded that rather than the total vibrational density of states, the vibrational modes spatially proximate to the OH species dominate the relaxation process.<sup>106</sup> Typical decay pathways for the OH stretch on SiO<sub>2</sub> ( $\nu_{\text{OH}} = 3750 \text{ cm}^{-1}$ ) were thought to involve the creation of four lower frequency quanta in the SiOH bend ( $\delta_{\text{SiOH}} = 970 \text{ cm}^{-1}$ ) or Si-OH stretch ( $\nu_{\text{Si-OH}} = 795 \text{ cm}^{-1}$ ) bands. In addition to OH adsorbates, experiments have characterized the CO( $\nu=1$ ) decay time in small metal carbonyls (e.g., Co<sub>4</sub>(CO)<sub>12</sub>) bound to SiO<sub>2</sub>.<sup>107</sup> A range of relaxation times from 100 to 400 ps was observed, depending on the specific metal carbonyl. For these SiO<sub>2</sub>-supported systems, multiphonon relaxation of the CO stretch mode ( $\nu_{\text{CO}} \approx 2080 \text{ cm}^{-1}$ ) to the bending ( $\delta_{\text{MCO}} \approx 550 \text{ cm}^{-1}$ ) and stretching ( $\nu_{\text{M-CO}} \approx 450 \text{ cm}^{-1}$ ) modes were considered to be important decay channels as was two-phonon emission to the Si-O stretch band ( $\nu \approx 1000 \text{ cm}^{-1}$ ) of the SiO<sub>2</sub> support. Generally it has been found that for high-frequency modes of molecular adsorbates on oxide surfaces  $T_1$  times lie in the range  $10^{-10}$ – $10^{-9}$  s, with relaxation occurring through multiphonon processes similar to those reported for isolated molecules. For these systems with slow  $T_1$  times, it has been found that many of the concepts developed in dilute solution and gas-phase energy-transfer studies can be applied in understanding the features controlling the rates and pathways of energy transfer.<sup>108</sup>

Experiments in the past two years have advanced to the stage where vibrational relaxation can be probed on single-crystal surfaces. The chemically prepared, ideally terminated H/Si(111)  $1 \times 1$  surface provides an elegant example of the range of information that can be extracted by combining time-resolved measurements with steady-state measurements on well-characterized surfaces.<sup>109,110</sup> Measurement techniques including FTIR, He atom scattering, scanning tunneling microscopy, and time-resolved infrared sum-frequency generation were used to characterize the adlayer surface. The time-resolved measurements were performed by pumping the Si-H vibration with a picosecond infrared pulse and probing the decay of the vibrational excitation with a time-delayed SFG probe. The experiments revealed a Si-H( $\nu=1$ ) vibrational recovery that was described by a single exponential response with  $T_1$  varying from 0.55 to 1.4 ns for surface temperatures from 460 to 95 K. The exceptionally long lifetime exhibited by this system was rationalized by the large energy mismatch between the excited Si-H stretch ( $2084 \text{ cm}^{-1}$ ) and the rest of the vibrational modes of the system: Si-H bend ( $637 \text{ cm}^{-1}$ ) and Si phonon modes ( $\leq 500 \text{ cm}^{-1}$ ). While the excited-state lifetime was substantially shorter than predictions of previous calculations, both theory and experiment support a multiphonon decay mechanism for this excited adlayer.<sup>111</sup> The measured temperature dependence of the vibrational relaxation rate together with knowledge of the Si-H bending and Si phonon frequencies

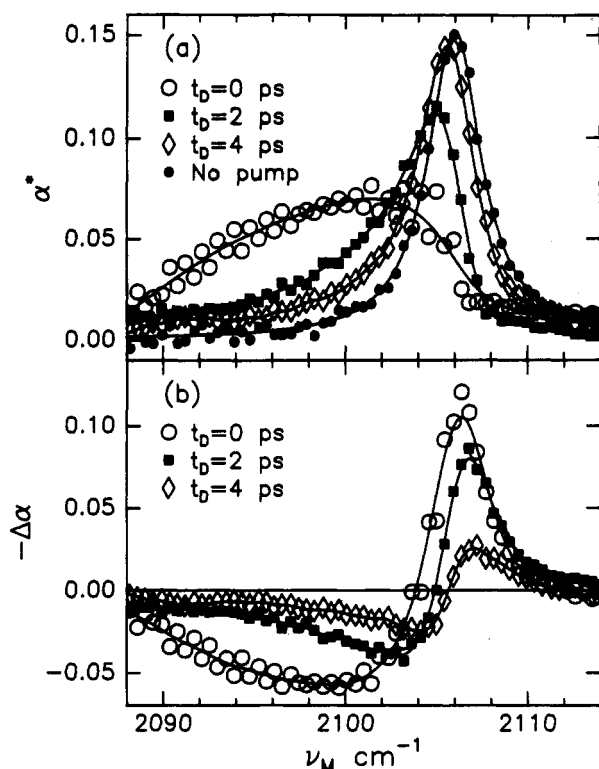
indicates that a four-phonon process is operative. Recent results by Harris and co-workers indicate that on vicinal surfaces coupling to step modes may critically influence  $T_1$  of Si-H vibrations on the terraces.<sup>112</sup>

The slow decay rates for these multiphonon processes reflect the energy mismatch between the excited mode and the modes that become energized in the damping process. Hence, in the examples cited above, the need to excite four quanta in the low frequency modes leads to slow damping rates. For the system CH<sub>3</sub>S/Ag(111), biexponential decay rates with time constants of 2.5–3 and 49–76 ps have been reported.<sup>113</sup> In these experiments, sum-frequency generation was used to measure the decay rate of vibrationally excited C-H stretch modes at  $2918 \text{ cm}^{-1}$ . Both components of the biexponential decay were interpreted in terms of intramolecular vibrational relaxation. The shortest decay time is thought to be due to Fermi resonances or anharmonic effects similar to those observed for hydrocarbons in solution where the excited CH stretch modes couple to the CH<sub>2</sub> bending modes.<sup>114</sup> The observation that the slow decay rate increased with temperature was consistent with the CH<sub>2</sub> bends ( $\nu = 1400 \text{ cm}^{-1}$ ) decaying by creating three phonons in lower frequency ( $\nu = 470 \text{ cm}^{-1}$ ) molecular modes.

In addition to clarifying the vibrational decay rates in these systems, measurements have begun to address the nature of the transient excited species on the surface. For the vibrationally excited H/Si(111) interface, spectral features due to two-phonon bound states of the Si-H stretching modes have been observed.<sup>115</sup> The simultaneous observation of distinct Si-H( $\nu=0 \rightarrow 1$ ) and Si-H( $\nu=1 \rightarrow 2$ ) transitions is expected when the anharmonicity of the individual Si-H bonds dominates the coupling between Si-H modes. By localizing the 0–1 and 1–2 excitations at the same adsorption site, the two-phonon bound state provides a practical analog to overtone pumping in small molecular systems. This valuable piece of spectroscopic evidence indicates that chemically significant amounts of vibrational excitation may be localized in particular surface bonds, either through sequential excitation ( $0 \rightarrow 1 \rightarrow 2$ , etc.) by laser pulses of appropriate duration and frequency or through less selective impact excitations by massive particles.

In addition to the characterization of the vibrational lifetimes,  $T_1$ , it is possible to use time-resolved techniques to access  $T_2$ , the vibrational dephasing time of the adlayer. Contributions to  $T_2$  (i.e., to the absorption bandwidth) arise from three sources: population decay ( $T_1$ ), pure dephasing ( $T_2^*$ ), and inhomogeneous broadening. This aggregate dephasing rate influences the time-domain response when the free induction decay<sup>116</sup> or the perturbed free induction decay<sup>117,118</sup> is measured. Since measurements that are controlled only by the overall  $T_2$  time cannot distinguish between the distinct physical contributions to dephasing, additional measurements are required that can differentiate between  $T_2^*$  and inhomogeneous broadening. The quantity  $T_2^*$ , of interest in terms of establishing the time scale for achieving phase coherent manipulation of surface reactions, is accessible through photon-echo measurements.<sup>119</sup> In the H-Si system, these measurements have shown<sup>115</sup> that  $T_2^*$  ( $85 \pm 7$  ps) is an order of magnitude shorter than  $T_1$  and that the inhomogeneous contributions to the line width dominate contributions from either  $T_1$  or  $T_2^*$ , even for very well ordered and oriented samples. The capacity to directly determine the different factors that contribute to the line widths of surface modes promises to greatly enrich the current understanding of energy-transfer processes at surfaces.

**Electronic Damping.** The most rapid adsorbate vibrational decay rates have been observed for the internal stretch mode of CO bound to metal substrates.<sup>120,121</sup> On both Cu(100) and Pt(111) surfaces, CO( $\nu=1$ ) is found to decay in  $\approx 2$  ps. The extremely rapid vibrational relaxation process can be seen in the differential infrared reflection spectra of Figure 7 taken synchronously with the excitation pulse and at delays of 2 and 4 ps.



**Figure 7.** Time-resolved infrared response for CO/Pt(111) at 150 K and  $\theta_{\text{CO}} = 0.5$  ML for three different time delays at a pump energy of 4  $\mu\text{J}$ . (a) Absorption,  $\alpha^*$ , for  $t_D$  values of (○) 0 ps, (■) 2 ps, (◇) 4 ps, and (●) no pump. (b) Transient difference spectra,  $-\Delta\alpha(\nu_M)$ , generated by subtraction of pump-induced absorption spectra from the absorption spectrum in the absence of the pump. The solid lines are fits to cubic splines (after ref 125).

The dramatic increase in relaxation rate for these systems, as compared to those surface layers dominated by multiphonon relaxation, has been attributed to decay through resonant creation of electron/hole (e/h) pairs in the metal. This relaxation channel, which promotes electron population of the metal from occupied states below the Fermi level to unoccupied states above the Fermi level, has no strict analog in molecular systems. Consequently, it is difficult to identify appropriate molecular models for the relevant energy transfer channels at metal surfaces. Two different models of the coupling to e/h pairs currently exist. One attributes the damping to an image dipole model,<sup>122</sup> while the other associates the coupling to charge transfer between the partially occupied  $\pi^*$  orbitals on the CO and electron density near the Fermi level.<sup>123,124</sup> In either case, it should be noted that due to the strong oscillator-to-metal distance dependence of both coupling schemes, as the distance between the metal substrate and the excited oscillator increases, the importance of coupling to e/h excitations will rapidly decrease. Hence, in adsorbates of increased size, as the vibrationally excited mode is positioned further and further from the surface, direct coupling to substrate free electrons will diminish and the adlayer will reach the limit where the local vibrational structure dictates the lifetime of the vibrationally excited system.

Substantially different behavior was observed in the transient spectrum of vibrationally excited CO on Pt(111) compared to that seen for H/Si(111).<sup>125</sup> Rather than the emergence of a distinct spectral feature characteristic of the  $\nu = 1 \rightarrow 2$  transition, the  $\nu = 0 \rightarrow 1$  mode was observed to gradually shift to lower frequency with increasing occupation of the excited state, as shown in Figure 7. A spectral response of this nature has been shown to be consistent with a system where the intermode coupling is comparable to or greater than the anharmonicity. In strongly coupled systems, a local mode description of the excited state properties (which is suitable for describing excited states for H/Si(111) and many molecules<sup>126</sup>) is inappropriate. The collective nature of the CO adlayer response should dramatically alter the

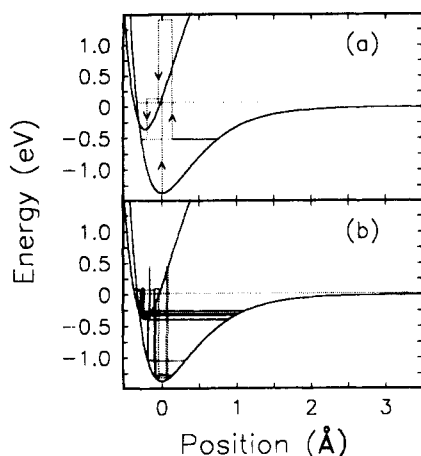
potential for excited-state chemistry. It should be noted that the H-Si and CO-Pt systems differ markedly in two distinct ways: the factor of 400 in the time scales for  $T_1$  and the relative strength of the adsorbate-adsorbate coupling compared to the anharmonicity of the respective oscillators. The lifetime difference reflects the operation of different mechanisms for coupling excited-state population to the substrate, while the spectroscopy of the excited state is essentially characteristic of couplings within the adlayer.

These measurements suggest that it will soon be possible to follow reactions having products that do not leave the surface with the same rigor as applied in state-resolved studies of desorbed species. By combining detailed analysis of product energy distributions and full characterization of the transient response of the adlayer, it should be possible to reach a much improved understanding of the factors that dominate energy transfer processes at surfaces. By simultaneously learning more about the mechanisms responsible for adlayer excitation and relaxation of excited adlayers, our ability to access novel surface chemistry through photoinduced processes should be greatly increased.

**B. Dynamics in the Surface Layer: Theory.** Theories of adsorbate vibrational relaxation are considerably more refined than those for ultrafast laser-induced dynamics. This is to be expected, since the comparison of theories for  $T_1$  and  $T_2$  processes to the widths and shifts of spectral features seen in surface vibrational spectroscopy (mostly IRRAS) has been continuing for about twenty years. Within the context of fitting non time-resolved spectroscopic data, theoretical approaches have recently been reviewed.<sup>127</sup> For adsorbates on metal and dielectric substrates, low frequency modes with  $\nu < 3\nu_D$  ( $\nu_D$  = substrate Debye frequency) are calculated to relax through anharmonic coupling in about  $10^{-12}$  s; reasonable anharmonic potential terms (cubic, quartic) can be chosen to reproduce most data.<sup>128</sup> Theoretical work on surface phonon relaxation (phenomenological  $T_1$ , classical dynamics, quantum dynamics) is closely related to that for multiphonon relaxation in solids,<sup>129</sup> intramolecular vibrational relaxation processes in molecules,<sup>130</sup> and molecular dynamics simulations of liquids.<sup>131</sup> At present, potential energy surfaces are not reliable enough to permit accurate predictions of multiphonon vibrational relaxation rates in the absence of experimental data. Along with the dynamics of OH/SiO<sub>2</sub> and H/Si(111), the relaxation of higher frequency modes of polyatomic molecules on metals (e.g., the CH stretch of CH<sub>3</sub>S/Ag(111)) may also be treated by multiphonon relaxation theories.<sup>111,113,132</sup>

For surface reactions that reflect electronic transitions, it is evident that account must be taken of the coupling of the electronic excited state(s) to the atomic motion characteristic of product formation. Quantitative theoretical treatments of this class of reaction will certainly require the availability of physically realistic excited state potential hypersurfaces.<sup>133</sup> At present, theoretical activity has begun by adopting approximate potential surfaces and then exploring different methods to treat the details of the adsorbate-excited electronic state coupling on a molecular level.<sup>134</sup>

Theoretical work emerging from AT&T Bell Laboratories has begun to show how a molecular orbital based approach can be applied to the problem of nonadiabatic adsorbate-metal coupling.<sup>124,135</sup> Recent efforts to treat molecular dynamics with electronic transitions (MDET) have focused on applying classical descriptions of atomic motions while self-consistently incorporating effects of electronic transitions. Initial efforts have been concerned with a description of the vibrational relaxation of CO bound to metal surfaces. When the Born-Oppenheimer approximation breaks down, the electrons can lag behind the nuclear motion such that the electron population near the Fermi level is modulated by the CO vibration. An appealing aspect of this approach is its ability to address the role of nonadiabatic damping of other normal modes of the adsorbate-surface system. The electron-vibration coupling terms that emerge from this work



**Figure 8.** Example of multiple excitation events in the DIMET model of femtosecond desorption of NO from Pd(111). The evolution of semiclassical trajectories is shown as transitions are made between the ground and excited potential surfaces for the molecule-surface coordinate (after ref 138).

provide values for the friction terms required for Langevin models of the molecular response in MDET systems. Since the same friction term can be used to mimic damping of vibrationally excited adsorbates and carrier-induced excitation of the adsorbate, this approach holds potential for addressing both vibrational lifetime problems and carrier induced reaction processes. Current activity in this area suggests that, at least for certain limiting cases, the application of classical Langevin techniques may provide useful insight into the chemical response to ultrafast surface events. The rate of desorption expected for an electronic temperature transient has, for example, been calculated within such a frictional coupling picture.<sup>136</sup> One intriguing notion has already emerged from explicit calculations of nonadiabatic coupling strengths. It appears that electronic excitations may be far more effective in stimulating desorption through the activation of frustrated rotational modes than through direct coupling to the adsorbate-surface vibrations.<sup>137</sup>

Other theoretical treatments of adsorbate response to optically induced surface transients are being explored at IBM.<sup>138</sup> Stimulated by the femtosecond laser desorption results described in the previous section, a model has been developed that addresses desorption induced by multiple electronic transitions (DIMET). This approach describes chemical events in which transient surface species generated by the leading edge of the laser pulse exhibit novel reaction probabilities as they subsequently interact with the trailing edge of the laser pulse. The nonlinear fluence dependence of the yield observed in femtosecond desorption experiments is consistent with such multiple excitations. The model is capable of describing both the highly nonthermal regime of conventional DIET processes and a pseudothermal regime in which the molecule-surface vibration is in equilibrium with the substrate electronic temperature which exceeds the lattice temperature. Figure 8 shows representative trajectories for motion on ground and excited surfaces during DIMET. The key scaling parameter defining the type of behavior is the ratio of the rate at which the multiple excitations occur to the rate of vibrational relaxation.<sup>139</sup>

These two models for molecular interactions with optically generated transients at surfaces serve to illustrate the rich and exciting status of the field while pointing to the clear need for strong interactions between theory and experiment. Both approaches seek to capture the key chemical steps that are involved in the short-time molecular response at the surface while providing sufficiently detailed predictions to permit experimental tests of the underlying coupling schemes.

## V. Future Trends

The short time available in which to induce a successful reaction following irradiation opens a number of opportunities for control of surface reactions. It may be possible to exploit the short lifetime to terminate reactions before they have a chance to proceed to undesired products. In the infrared spectral region, current and emerging laser technology will enable examination of molecular dynamics at surfaces ranging from the diffusion and reorientation of adsorbates, to their isomerization and resonant desorption. In addition, substrate mediated effects will be accessible through the infrared excitation of carriers in both narrow-gap and metallic substrates. When the opportunities provided by visible and ultraviolet lasers are included, the potential for selective deposition and desorption, and for probing charge transfer processes at buried interfaces is evident. The lifetimes of the excited states are clearly in the picosecond (or less) regime, such that application of experimental and theoretical approaches described herein will directly address optically driven events at chemically modified surfaces.

To date, the overwhelming majority of photochemical processes at surfaces have been restricted to coupling of the ground state to a single excited state. The potential of exploiting transient absorptions in one excited state to allow photons of a second wavelength to access new excited states is well-known both in gas-phase double resonance experiments and in two-photon photoemission. In the near future, application of these methods to selectively up-pump the excited species to achieve new reaction products will undoubtedly be explored. By exploiting the optical properties of the initial transient, it may be possible to introduce a second pulse of a different color to achieve new surface reactions. Preliminary examples of the excited state spectroscopy and dynamics that will be possible are seen in the H-Si and CO-Pt vibrational relaxation studies in the previous section. While the successful implementation of such interactions requires the knowledge of multiple excited-state potential surfaces, much of the theoretical framework for dealing with the evolution of population on these excited-state surfaces is already in place.<sup>140,141</sup>

For reaction mechanisms where chemical bond rupture occurs on the pico- or femtosecond time scale, the ability to account quantitatively for the energy content of the adsorbate/substrate system will be a tremendous asset to establishing the nature of the potential energy surfaces involved. Under conditions of prompt desorption, the nascent products provide a sampling of the evolution from bound species to free molecules. By combining time-resolved probes of energy transfer within an adsorbed layer and detailed characterization of product energy distributions, the potential for mapping out the relevant potential energy surfaces will be significantly advanced. Efforts to account for energy redistribution in all the degrees of freedom, including both electronic and nuclear, will require new theoretical developments.<sup>142</sup>

## VI. Summary

Surfaces have frequently been associated with the rapid quenching of molecular excited states. Yet, as demonstrated in section II of this article, the presence of strong interactions between adlayers and the underlying substrate can introduce new reaction channels that do not exist in the case of free molecules. In those instances where the reaction of interest proceeds on a sufficiently short time scale, reaction channels may successfully compete with quenching channels. The increase in the number of reaction channels and the ability to exploit surface-mediated quenching to restrict reaction products to those attainable on a picosecond time scale, contribute to the promise of attaining novel, non-equilibrium reaction products through photochemical processes at surfaces.

It is readily apparent that for a wide range of nonequilibrium reactions at surfaces, the events that transpire within the first

few picoseconds of the system being excited define the ultimate reaction products. Our ability to characterize these prompt energy-transfer events is rapidly developing. As insight into the critical time scales and pathways for energy flow increases, it is reasonable to anticipate that new applications for surface modification through nonthermal processing will emerge.

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