Laser-stimulated desorption from surfaces
Katharina Al-Shamery and Hans-Joachim Freund*

Recent experimental and theoretical results focus on nonthermal laser-induced desorption after UV-laser excitation with the aim of obtaining insights into microscopic processes, including the relevant potential energy surfaces and lifetimes of the excited states that are involved. Results range from measurements and interpretation of quantum state resolved studies to femtochemistry.

Introduction
Solid surfaces can be used as instruments to orient and modify molecules at distances close to molecular bondings, while light may serve as a tool to start reactions between neighbor molecules. Such photochemical reactions are known to be important in many systems in nature ranging from the formation of larger chiral organic molecules in prebiotic systems [1] to reactions at small particles, like ice or dust in the atmosphere [2]. Laser induced processes are used in technical applications such as laser microtechnology to build microelectronic, optical, optoelectronic, and micromechanical devices [3], in photocatalysis and in photoelectrochemistry [4].

One of the advantages of using light to start a chemical reaction is its potential for selective reaction control. As electronically excited states, particularly on metals, have lifetimes of only a few femtoseconds before being quenched, a direct control using ‘pump and control’ techniques as in gas phase reactions is scarcely possible. By choosing the appropriate surface, however, one may not only be able to alter the catalytic activity but also to control the excited state lifetime intrinsically. Therefore a detailed understanding of the underlying elementary processes of electronic and nuclear motion and the related timescales is unavoidable if we are to use the full potential of such an approach. As will be seen below, even for simple reactions the processes can be rather complex. Therefore the investigations in fundamental research concentrated mainly on the most simple chemical reaction, the breaking of the molecule-surface bond followed by the desorption of the molecule. This review will focus on this particular aspect, particularly on UV-laser induced processes. A good overview of the major recent activities in the field can also be obtained from a number of reviews, special journal issues, books and conference proceedings published during the past year [5*6,7*8*10*].

Experiments
The desorption processes can be classified according to how the final excitation of the adsorbate can be achieved. A primary excitation can be a vibrational or electronic excitation of the adsorbate itself followed by relaxation processes and nuclear motion with energy transfer into the molecule-surface bond. If the amount of energy is large enough to overcome the potential energy barrier of the molecule-surface bond the molecule will desorb. There are, however, only a few examples in the literature for such a direct process. It can be identified if the desorption efficiency follows the absorption spectrum of the adsorbate or, if this spectrum is very weak, if the polarization-dependent desorption cross sections (measured as a function of the incident angle) deviate from that of the substrate absorbance. One recent example of this type of identification is the UV-laser induced desorption and dissociation of methane on Pt(111) studied by Watanabe et al. [11].

The majority of excitations have been shown to result from secondary processes. The primary electronic excitation step for a large number of systems including metals, semiconductors and transition metal oxides as substrates is the formation of excited charge carriers within the substrate. One important step then is the diffusion of the carriers to the surface and their temporal localization at the reaction site, that is to say coupling to the adsorbate system. Such a coupling is often thought to be accompanied by the formation of a negative intermediate ion with a partial or complete transfer of the electron into an unoccupied adsorbate state. As the free electron gas of the substrate quickly quenches electronically excited states, those intermediate states have very short lifetimes, down to a few femtoseconds for metals. As the majority of molecules desorb as neutrals the transfer back of the electron has to precede the desorption. Desorption can only occur if enough potential energy in the intermediate excited state has been transferred into the kinetic energy of nuclear motion within the molecule–surface coordinate. This model for desorption is known as the Menzel–Gomer–Redhead (MGR) model [12*]. We shall discuss a number of experiments connected to such a process below.

A different secondary process has been demonstrated very recently for the system O2/Ag(110) by Xin and Zhu [13*]. The molecules may not necessarily desorb but may be displaced on the surface. Localized collisions can occur
with momentum transfer to other molecules which may then desorb.

A further secondary process is due to a scattering of the created charge carriers with the substrate phonons. As a result a temperature jump within the surface can cause chemical reactions. Thermal desorption is not only a major process in microtechnology [3] but is also used in analytical chemistry to mildly desorb intact molecules of very large sizes (up to several hundred thousand mass units) for laser mass spectroscopy, as has been discussed in the review by Zenobi [14].

As can already be seen, the simple desorption process may be rather complex. Laser-induced reactions followed by desorption of some of the products as investigated by the groups of Polanyi, Simpson, Stair and Osgood [15*,16,17*,18], are even more complicated. Recent examples have demonstrated that the surface photodissociation dynamics are strongly altered from the gas phase; however, the major problem is the fact that the conditions may change during the reaction as the products remaining on the surface may influence and modify the electronic and geometrical properties of the surface. This is one of the reasons why those reactions are not understood in as much detail as the simple desorption processes.

If one wants to obtain a more detailed insight into the desorption dynamics, two different experimental approaches can be distinguished which include final state distribution measurements and real time experiments. Recently a successful approach has been shown to stem from a careful characterization of the initial adsorbate state connected with a detailed investigation of the efficiency of desorption and final state distributions of desorbing molecules. The latter are measurable parameters which directly result from the relevant potential energy surfaces involved and lifetimes within them. When these data are combined with extended theoretical calculations one can obtain insight into details of the desorption dynamics. While the early experiments concentrated mainly on measuring final state distributions of atomic or diatomic molecules people started to extend experiments towards more complex molecules a few years ago. The detection of the internal quantum state distributions of NH₃ photodesorbed from Cu(111) at 6.4 eV by Hasselbrink's group may serve as an example [19*] (see Fig. 1). A geometry change within the excited state is revealed in which the symmetric out of plane bending vibration is involved. The data help to interpret pronounced coverage-dependent isotope effect in the desorption yield observed by Hertel et al. [20*].

More elaborate studies than the usual detection of scalar values such as translational, rotational and vibrational final state distributions have also been reported during the past year for the desorption of diatomic molecules. These investigations are now being extended toward directional aspects. While measurements on angular distributions of desorbing molecules have existed since the very early days of photodesorption experiments, the first experiments have recently been carried out to obtain the alignment of the angular momentum of the desorbing molecules. It is somewhat surprising that this aspect has been neglected for laser induced desorption as it is standard in gas phase photodissociation dynamics and scattering processes. Such experiments are particularly valuable, as pronounced rotational alignment effects can reveal details about geometry changes during the excitation. Results on the nonthermal desorption processes of CO from Si(100) by Zimmerman and Ho [5*] and our own results

**Figure 1**

Quantum state resolved detection of complex molecules: NH₃/Cu(111). Overview of the v₂ progression (symmetric out-of-plane bending mode) in the (2+1) REMPI (resonance enhanced multiphoton ionization) spectrum (via B -> X) of NH₃ in the gas phase at 300K (lower trace) and of NH₃ photodesorbed from Cu(111) with 6.4 eV at T=130K (upper trace). The relevant vibrational bands are indicated below x-axis. The average energy content in the v₂ mode corresponds to a temperature of T vib =1000 K with a marked underpopulation of the antisymmetric v₂ and a rotational temperature close to the surface temperature (no torque during desorption). The results indicate that energy required for desorption is transferred from the initial electronic excitation to the molecule-surface bond via the intramolecular coordinate v₂. Reproduced with permission from [19*].
on Cr$_2$O$_3$(0001) \cite{21*} have been published. A strong velocity and rotational quantum number dependence of the alignment showing a change from helicopter (angular momentum parallel to the surface normal) to cartwheel (angular momentum perpendicular to the surface normal) modus with increasing rotational quantum number has been observed in both cases, indicating the involvement of multidimensional potential energy surfaces, particularly those of the hindered rotation, implying a geometry change and torsional vibration (see Fig. 2).

Figure 2

Rotational alignment of desorbing molecules: CO/Cr$_2$O$_3$(0001). A spatial distribution of J vectors with respect to the surface normal Z, in other words rotational alignment, can be described by a series of multipole moments for which the quadrupole moment is the dominating parameter $<\mu^2>/2 <\mu J Z>$ with $12 <\mu J Z> < 2$. The figure shows the change of the quadrupole moment, that is to say the change of the rotational alignment from helicopter (J Hz) to cartwheel (J Hz) modus as a function of the rotational quantum number for different translational and vibrational excitation of CO desorbing from Cr$_2$O$_3$(0001) (filled dots: $v''=0$, $v=1160$ m/s; filled triangles: $v''=0$, $v=340$ m/s; open rhombs: $v''=1$, $v=1160$ m/s). The data can be interpreted as due to a geometry change from flat to bent configuration during the desorption. Reproduced with permission from \cite{21*}.

New and interesting results have been obtained even for such simple systems as the desorption of atoms. Itoh’s group \cite{22*} has used scanning tunneling microscopy to investigate the site selectivity for desorption, which they recently demonstrated for the laser-induced bond breaking of the adatoms of the Si(111)-7x7 surface (Fig. 3).

Figure 3

Site selective desorption: adatom desorption of the Si(111)-7x7 surface. Tunneling image (bias voltage -2.0 V) of the Si(111)-7x7 surface (a) before and (b) after irradiation with laser pulses of 2.48 eV (300 mJ cm$^{-2}$) which shows the site selective increase in adatom site vacancies after laser irradiaion. Reproduced from \cite{22*} with permission.

In a second type of experiment, real time measurements on certain details of the desorption process have been carried out. A large number of papers have focused on the real time electron dynamics of semiconductors in other words the substrate excitation alone because there is also a strong interest with respect to optoelectronics. One reason for the interest is that the sizes of electronic devices approach scattering lengths of electrons; another is a future use of femto second lasers with ultrafast optoelectronic...
elements. We will only mention a recent review of this particular field by Haight [23*] (see Fig. 4).

Figure 4

Hot-electron relaxation dynamics due to electron-electron scattering of Cu(100) with <15 fs time-resolution. Pump-probe measurements of hot-electron dynamics at E=1.7eV and 3.2eV recorded with laser pulses of less than 15 fs pulse length. The measured photoemission intensity is given as a function of delay between pump and probe pulse. The baseline corresponds to times longer than electron relaxation dynamics. Solid lines are fits taking coherent (insitu measurement of the effective system response function) and incoherent components into account. The dotted line is a fit of the 3.2 eV data to a Gaussian function. Lifetimes obtained are 52±8 fs (1.7 eV) and 17±3 fs (3.2 eV). Reproduced from [40**] with permission.

Time-resolved two photon photoemission is used as an experimental tool in order to study the time evolution of the occupation of initially unoccupied adsorbate states. The first publications on the system CO/Cu(111) have come from Knoesel et al. [24*]. As the lifetimes of such states are extremely short, as yet only estimates from correlation techniques of the upper limit are possible for the lifetime of the 2π* resonance of CO which is in the range of <20 fs.

The absorption coupling strengths between different degrees of freedom are essential within the desorption process, particularly those of vibrational modes and low-lying electronic states as studied by Cavanagh et al. [25**] and Culver et al. [26]. Cavanagh et al. [25**] for example have summarized their recent work on the systems CO/Pt(111) and CO/Cu(100) and presented experimental results on the temporal evolution of the CO stretch after ultrashort IR, visible and UV excitation obtained from picosecond and femtosecond IR techniques together with current models of the damping rates (see Fig. 5).

Figure 5

Adsorbate response to substrate heating for CO/Cu(100). Time dependence of the transient response of CO/Cu(100) of the internal CO stretching absorption to visible and ultraviolet pumping as a function of delay time t_d for (a) 578 nm pumping, T=150K, v=2085 cm⁻¹ (offset by 0.03 for clarity). (b) 578 nm pumping, T=100K, v=2087 cm⁻¹ (c) 289 nm pumping, T=100K, v=2087 cm⁻¹. The signal peaks near t_d=0 and decays quickly to an intermediate value, and then slowly decays on a 200 ps time scale. The initial time constants for the signal to decay are 2.60±4 ps (100K, visible), 2.30±3 ps (100K, UV) and 2.30±4 ps (150K, visible). The dashed curve represents the autocorrelation of sech² pulses with 1.2 ps FWHM (full width at half maximum) duration. The data agree with an anharmonic coupling of the stretching vibration to the frustrated translation (ν=32 cm⁻¹) which changes in population due to coupling to the photogenerated hot electrons and to the heated phonons (compare with Table 1). Reproduced from [41**] with permission.

The role of nonequilibrium electrons has been studied by Ho and his group [27*] by recording time-resolved velocity distributions of O₂ after femtosecond laser desorption from Pt(111). The surface femtochemistry of O₂ and CO on Pt(111) has been investigated by Deliwala et al. [28*] in more detail than in previous experiments by systematically varying the fluence and pulse length for pulse lengths between 80 fs and 3.6 ps. The role of non-thermalized electrons and the influence of preheating of the surface modes is shown. The sharply increased desorption yield of O₂ with respect to CO₂ desorption is interesting for this type of experiment.

Theory

A strong step towards a detailed comprehension of laser induced desorption comes from very recent theoretical progress. The first quantum mechanical calculations which
describe the potential energy surfaces of electronically excited states on an *ab initio* basis have been published [29*,30**]. Murata's group has investigated the system CO/Pt [29*] while our own group has worked on NO/NiO(100) [30**]. In contrast metal-adsorbate systems, for which serious convergence problems with respect to the cluster size are quite common in cluster calculations, relatively small clusters are sufficient to allow a quite accurate, quantitative description of oxide surfaces. This is because of the strong ionicity of such systems and related, rather local, metal ion orbitals. A particularly suitable system for these elaborate calculations turned out to be the system NO/NiO(100) for which high quality CASSCF-CI calculations (complete active space self-consistent field and configuration interaction) have been performed [30**]. The calculations of Klüner *et al.* [30**] revealed that the major excitation step ends in a complete transfer of an electron from the O 2p-orbitals to the NO 2π-orbitals with strong electrostatic interactions due to this ion pair formation, a finding which might be quite general for adsorbate-substrate systems with dominating initial electrostatic interactions (see Fig. 6).

A second type of theoretical calculations is concerned with dynamical calculations such as wavepacket calculations which reveal the lifetimes of excited states and reproduce the final state distributions [31,32,33]. The system NO/Pt(111), for which extensive experimental studies exist, has been used as a model system for a number of such calculations to describe photodesorption. Saalfrank [31] has described three one-dimensional models of increasing complexity to compute observable quantities such as desorption probabilities, time-of-flight spectra, etc.

Two-dimensional wavepacket calculations within model potentials that include the intramolecular vibration in addition to the center-of-mass translational excitation has been presented by Chakrabarti *et al.* [32]. They performed these calculations in order to obtain desorption probabilities and vibrational populations. Their calculations are consistent with a lifetime in the range 20–60 fs, which is surprisingly long.

An interesting new approach is discussed by Holloway's group [33] who treated the motion of the molecule and the hot electron (which temporarily resonates with an unoccupied molecular orbital) on an equal footing in their time-dependent two dimensional quantum wavepacket calculations. By systematically varying the model potentials they found that desorption is even possible for lifetimes less than 1 fs for moderately excited state potentials.

The first calculations have been presented for the more complex photodissociation process. Hintender *et al.* [34*] discuss the photodissociation of HCl adsorbed on MgO(001) by classical molecular dynamics of a single adsorbate system, including the substrate phonon

![Figure 6](image)

*Ab initio* potentials of electronically excited states of NO/NiO(100). Plot of the manifold potential curves of the different types of excited states of NO $\text{NiO}_2^-$ embedded in an unmodified Madelung field (a cluster modelling NO/NiO(100)) obtained by CASSCF-CI (complete active space self-consistent field and configuration interaction) *ab initio* calculations. (1) Ground state and $d-d$ excitations with a distance behavior similar to that of the ground state. (2) $\text{O}_2^\text{p}$ Ni 3d charge transfer states with a distance behavior similar to that of the ground state. (3) Cluster NO charge transfer states with a distance behavior dominated by a strong Coulomb attraction; this is relevant for the photodesorption process. The a.u. label indicates atomic mass units. (Work from H-J Freund's group, reprinted with permission from [30**].)
the initial translational and librational excitation. Stace [37] has presented a phenomenological model to simulate a vibrationally excited molecule that is weakly coupled through a damped harmonic oscillator to an energy sink in order to ascertain under which conditions a true RRKM (Rice–Ramsperger–Kassel–Marcus) unimolecular reaction is possible on a solid surface.

The interesting new phenomena of femtosecond-pulse laser desorption, in contrast to nanosecond-pulse laser desorption, have challenged theoreticians to develop new theoretical approaches. One example is the occurrence of a strong nonlinear fluence dependence of desorption yields, which is related to the creation of highly equilibrated substrate electrons. Brandbyge et al. [38**] have discussed how the energy of highly excited electrons is transferred into the adsorbate center-of-mass degrees of freedom by a direct coupling mechanism. They describe desorption with a model in the language of an effective friction of electronic origin and an associated fluctuation force which induces an impulsive force on the nuclei. This model has been applied by Springer and Head–Gordon [39**] to simulate the femtosecond laser-induced desorption of CO from Cu(100) in the high coverage regime. Their calculations shine light onto the role of momentum in the plane of the surface; momentum leads to collisions, and Springer and Head–Gordon’s calculations shine light onto this process and also onto energy pooling pooling between molecules in the overlayer (see also Table 1 for work related to Fig. 5).

<table>
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<th>Mode</th>
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<th>(t_{\text{phonon}})(ps(^{-1}))</th>
<th>(t_{\text{electron}})(ps(^{-1}))</th>
<th>(t_{\text{OH}})(ps(^{-1}))</th>
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<td>1.7</td>
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<tr>
<td></td>
<td>150</td>
<td>&gt;1000</td>
<td>1.8</td>
<td>1.6</td>
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<td></td>
<td>450</td>
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<td>1.5</td>
</tr>
<tr>
<td>CO surface stretch</td>
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<td>41.0</td>
<td>22.0</td>
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<tr>
<td></td>
<td>150</td>
<td>9.7</td>
<td>9.2</td>
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<td></td>
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*Extract from Table III in [42]. \(^{1}\) Lifetimes are obtained with phonon relaxation only (no electronic friction), with electronic relaxation only (with the copper surface assumed to be rigidly fixed), and with both channels.

Conclusions

Our review clearly shows that recent developments in the field of laser induced desorption tend to use a great variety of experimental and theoretical approaches in order to learn about photodesorption dynamics. Experimental techniques have been introduced to detect quantum state resolved final state distributions of molecules larger then two atoms, to study stereodynamics and to learn about size specificity with the use of microscopical techniques of atomic resolution. There are exciting experiments using femtosecond and picosecond lasers which open up time domains in the order of the desorption process itself. New effects resulting from highly excited nonequilibrium electrons have been observed. Both experimental and theoretical results clearly indicate that in most processes more than one molecular degree of freedom of the adsorbate is relevant for the laser-induced desorption process. It is exciting that the first high quality quantum chemical calculations of electronically excited states are now available. It is only a question of time before multidimensional wavepacket calculations will be performed within those potentials so that the remaining ambiguities related to the choice of the model potentials used up to now can be cleared, particularly those ambiguities concerning lifetimes of excited states. New models have been developed to describe femtosecond experiments. Femtochemistry will certainly be one of the major topics within the field in the future.

Acknowledgements

The authors wish to thank T Klüner for valuable comments. KA is grateful for financial support from the Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen in the form of a Lise-Meitner fellowship. The authors also wish to thank the Deutsche Forschungsgemeinschaft, the Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen and the Fonds der chemischen Industrie, who supported their work.

References and recommended reading

Papers of particular interest, published within the annual period of review, have been highlighted as:

- of special interest
- ** of outstanding interest


This review gives a thorough overview of the state-of-the-art of laser based quantum state resolved studies on photophysical surface processes including studies on metal, semiconductor and insulator single crystal surfaces.

Table 1

Temperature dependence of the vibrational lifetimes of the modes of CO on Cu(100) calculated using stochastic dynamic simulations with electronic friction to self-consistently incorporate phonon and nonadiabatic electron-hole pair mechanism of energy dissipation.*
The main developments up to 1996.

This retrospective view by one of the fathers of the MGR model describing how it came about and what the authors present results on adatom desorption from Si(111)-7x7 using scanning tunnelling microscopy. Such a combination of laser technology with in-situ measurements on the desorption process gives an entertaining, but at the same time instructive, view of the model so familiar to everybody in the field and on the developments which the model initiated. The article demonstrates that even 30 years after the development of the model it has not lost any of its strength.

The system presented 'hot' oxygen atoms are created during photodissociation of surface dioxygen. To follow the main step of laser induced desorption, the coupling of a hot charge carrier process is recommended to anyone interested in processes on all aspects of dynamical quantum processes on solid surfaces within the years 1995 and 1996.

The high vibrational excitation of the desorbing NO is related to the differences of solid-liquid interfaces in comparison to solid-gas interfaces; and the coupling of electronic degrees of freedom across interfaces of metals and semiconductors. Model studies under ultrahigh vacuum conditions are presented as well as insitu measurements.

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Pump-probe techniques using femtosecond laser pulses are used by the authors to study the velocity distribution of O2 photodesorbed from Pt(111) as a function of laser fluence and thus substrate electronic temperature.

The authors present results on the vibrational predesorption of CO and CH3F molecules physisorbed on NiO(100) using a 2D model and classical chaotic dynamics. The advantage of this method is that the time dependence of such an inefrequent process as vibrational predesorption can be easily treated on much longer time scales than within usual quantum mechanical calculations. The presence of dynamical barriers in the phase space are revealed in multiple peaks which appear in the calculated time of flight spectra.

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Surface photochemical reactions are rather complex. Thus theoretical treatments are difficult and therefore very valuable. Such a detailed study using classical molecular dynamics is presented for the photodissociation dynamics of H2O/MgO(001) by the authors. A quantum effect is accounted for by taking the hydrogen coordinates and momenta in the initial state from a Madelung potential used to be obtained by another technique.


The authors are leaders in the field of model developments to describe femtosecond-pulse laser desorption. How energy is transferred by a subpicosecond temperature pulse on the order of 5000K in the substrate-adsorbate electron system to the adsorbate center-of-mass degree of freedom by a direct coupling mechanism is treated via an effective electron friction and associated fluctuating force.


The purpose of this elaborate paper is to investigate the effect of coverage on desorption yield, properties of the desorbed molecules, and the mechanism of femtosecond laser-induced desorption for the system CO/Cu(100). The authors use a multidimensional generalization of the fractional model in which the frictional kernel is evaluated by electronic structure calculations.


The authors present state of the art measurements on the femtosecond dynamics of hot-electron relaxation in Cu(110) and Cu(100) using ultrafast laser pulses (<1 fs) employing time-resolved photodissociation spectroscopy. The dependence of hot-electron thermalization by electron-electron scattering is studied as a function of laser polarization and photon energy. The population decay rates are 6.5 times slower than those predicted by the Fermi liquid theory.


The authors present thorough time-resolved experiments on the infrared response of CO/Cu(100) to heating of the substrate under static and transient temperature conditions. Transient frequency shifts of this mode are shown to result from rapid increase and decrease of the population of the frustrated transition to which the CO stretching is anharmonically coupled. The results are consistent with models based on an elastic continuum model of vibrational coupling, but disagree with models relating the change of surface reflectivity or electrical resistance to damping of the frustrated transition.