Laser-stimulated desorption from surfaces
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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.

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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 $O_2/Ag(110)$ 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 NH_3 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: NH_3/Cu(111). Overview of the v_2 progression (symmetric out-of-plane bending mode) in the (2+1) REMPI (resonance enhanced multiphoton ionization) spectrum (via B ←X) of NH_3 in the gas phase at 300K (lower trace) and of NH_3 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 v_2 mode corresponds to a temperature of T_{vib}=1000 K with a marked underpopulation of the antisymmetric v_2 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 v_2. Reproduced with permission from [19*].
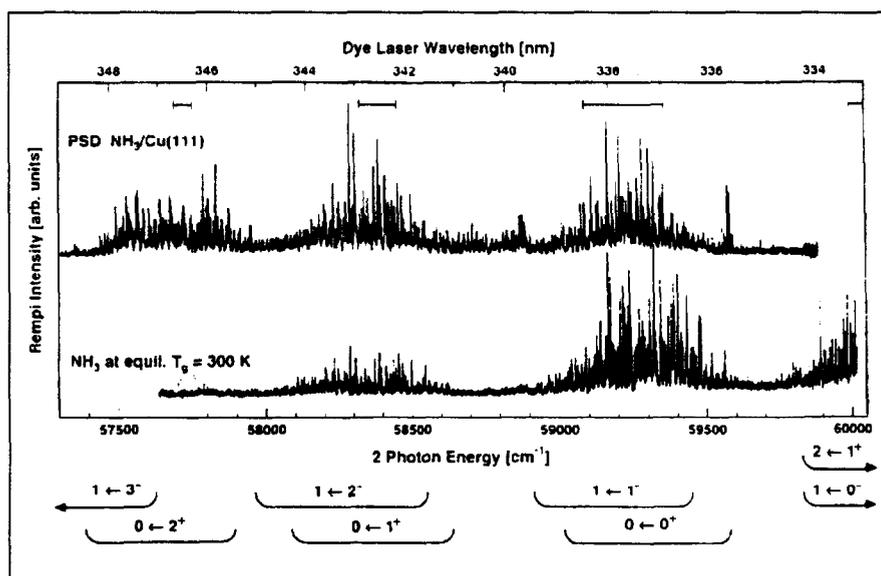
on $Cr_2O_3(0001)$ [21*] have been published. A strong velocity and rotational quantum number dependence of the alignment showing a change from helicopter (angular momentum parallel to the surface normal) to cartwheel (angular momentum perpendicular to the surface normal) modus with increasing rotational 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
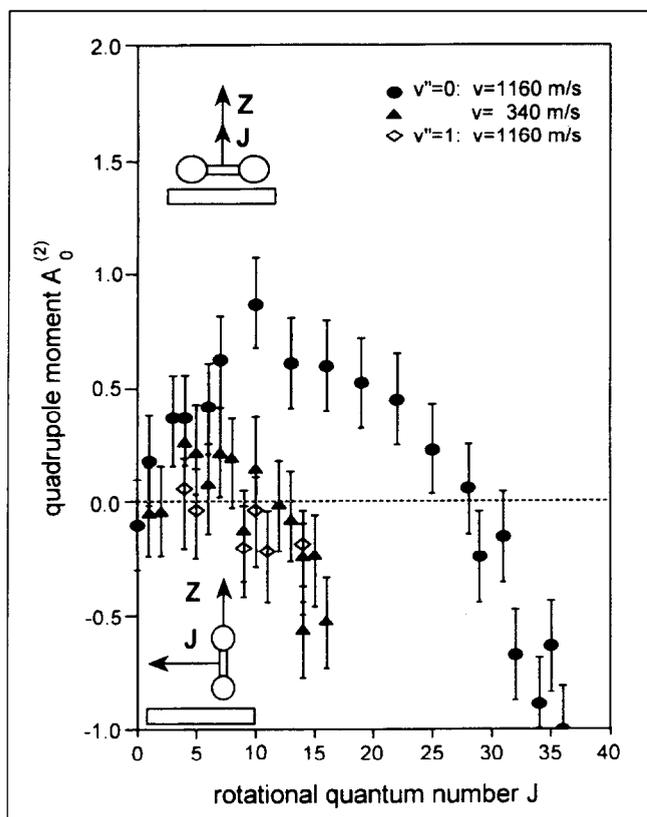
Rotational alignment of desorbing molecules: $CO/Cr_2O_3(0001)$. A spatial distribution of **J** vectors with respect to the surface normal **z**, in other words rotational alignment, can be described by a series of multipole moments for which the quadrupole moment is the dominating parameter $(A_0^{(2)} = 2 < P_2(J \cdot z) >$ with $-1 \leq A_0^{(2)} \leq 2)$. The figure shows the change of the quadrupole moment, that is to say the change of the rotational alignment from helicopter (**J** ‖ **z**) to cartwheel (**J**⊥**z**) modus as a function of the rotational quantum number for different translational and vibrational excitation of CO desorbing from $Cr_2O_3(0001)$ (filled dots: $v''=0$, $v=1160 ms^{-1}$; filled triangles: $v''=0$, $v=340 ms^{-1}$; open rhombs: $v''=1$, $v=1160ms^{-1}$). The data can be interpreted as due to a geometry change from flat to bent configuration during the desorption. Reproduced with permission from [21*].

New and interesting results have been obtained even for such simple systems as the desorption of atoms. Itoh's

group [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
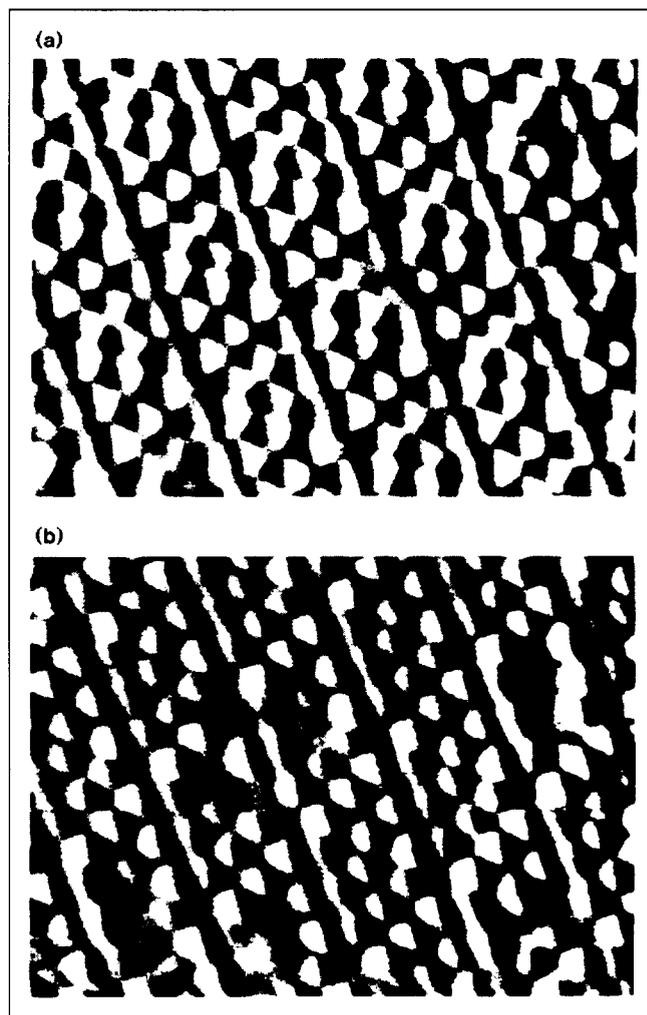
Site selective desorption: adatom desorption of the Si(111)-7x7 surface. Tunneling image (bias voltage −2.0 V) of the Si(111)-7x7 surface **(a)** before and **(b)** after irradiation with laser pulses of 2.48 eV (300 mJ cm^{-2}) which shows the site selective increase in adatom site vacancies after laser irradiation. Reproduced from [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
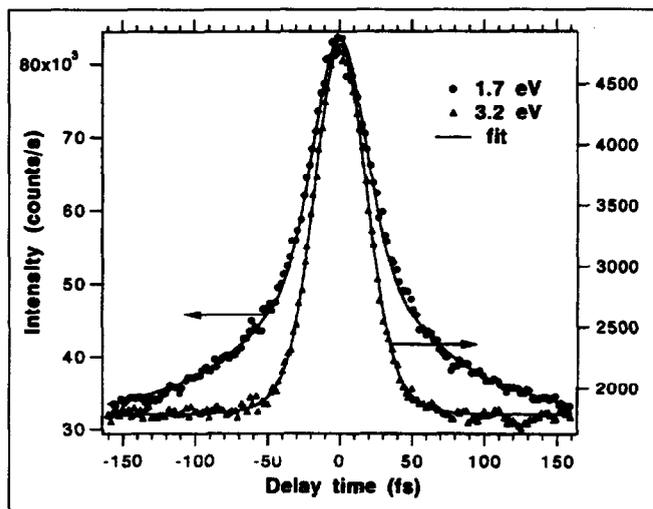
Hot-electron relaxation dynamics due to electron–electron scattering of Cu(100) with <15 fs time-resolution. Pump-probe measurements of hot-electron dynamics at $E = 1.7$ eV and 3.2 eV recorded with laser pulses of less than 15 fs pulse length. The measured photoemission intensity is given as a function 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 $2\pi^*$ 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
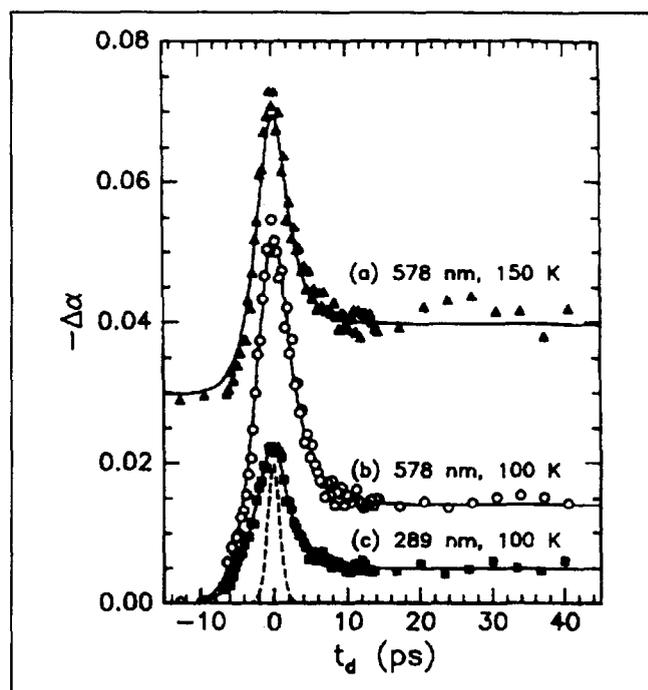
Adsorbate response to substrate heating for CO/Cu(100). Time dependence of the transient response of CO/Cu(100) of the internal CO stretching absorption to visible and ultraviolet pumping as a function of delay time t_d for (a) 578 nm pumping, T=150K, $v=2085$ cm^{-1} (offset by 0.03 for clarity). (b) 578 nm pumping, T=100K, $v=2087$ cm^{-1} (c) 289 nm pumping, T=100K, $=2087$ 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 sech^2 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 ($v=32$ 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 O_2 after femtosecond laser desorption from Pt(111). The surface femtochemistry of O_2 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 O_2 with respect to CO_2 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/Pt₂ [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 calculation, 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
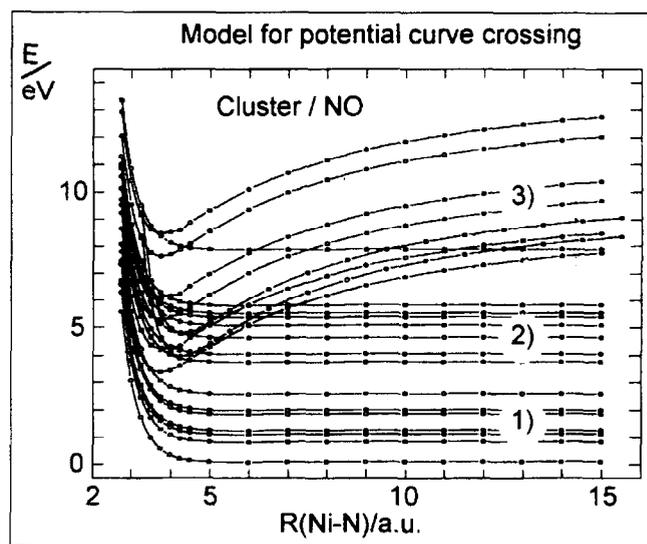
Ab initio potentials of electronically excited states of NO/NiO(100). Plot of the manifold potential curves of the different types of excited states of NO NiO₅⁸⁻ embedded in an unmodified Madelung field (a cluster modelling NO/NiO(100)) obtained by CASSCF-CI (complete active space self-consistent field 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)** O2*p* Ni 3*d* 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**].)

modes to simulate angular distributions of the scattered photofragments, which show characteristic rainbows, scattering shadows, and resonances.

Some recent papers have been concerned with describing the nonthermal desorption, in other words the predesorption after vibrational excitation of physisorbed systems such as CO adsorbed on NaCl(100) [35*,36,37]. Although such studies stem from the very early days of laser-induced desorption, this field has been neglected experimentally as most processes observed so far have been due to thermal heating of the surface instead of nonthermal processes. With the progress made in femtochemistry, however, this field may see a revival, for which reason we include it here. Brivio *et al.* [35*] have used the phase space properties of 2D classical Hamiltonian nonlinearly coupled models to calculate the time-of-flight spectra for elastic predesorption of CO and CH₃F·from NaCl(100). They have demonstrated the presence of bottlenecks in the phase space induced by the chaotic Hamiltonian dynamics. Three-dimensional time-dependent quantum calculations have been performed by Dzegilenko and Herbst [36] to study the dependence of the strong coupling among the translational, physisorption and vibrational degrees of freedom of CO on NaCl(100) on

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).

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 site 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

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.*

Mode	T(K)	$\tau_{phonons}(ps^\dagger)$	$\tau_{electrons}(ps^\dagger)$	$\tau_{both}(ps^\dagger)$
CO internal	10	>1000	2.0	1.7
stretch	150	>1000	1.8	1.6
	450	>1000	1.5	1.5
CO surface	10	26.0	41.0	22.0
stretch	150	9.7	9.2	4.8
	450	4.0	3.4	1.6
Frustrated	10	>50.0	1.0	1.0
rotation	150	6.0	0.8	0.8
	450	2.5	0.6	0.6
Lateral	10	>50.0	44.0	14.0
frustrated	150	9.7	23.0	4.0
translation	450	3.7	5.9	1.5

*Extract from Table III in [42]. †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.

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

1.   Bourdon EB, Das P, Harrison I, Polanyi JC, Segner J, Stanners CD, Williams RJ, Young PA: **Photodissociation, photoreaction and photodesorption of adsorbed species.** *Faraday Discuss Chem Soc* 1986, **82**:343–358.

2.   Ramaker DE: **Comparison of photon-stimulated dissociation of gas-phase, solid and chemisorbed water.** *Chem Phys* 1983, **80**:183–202.

3.   Metev SM, Veiko VP: in *Laser-assisted microtechnology.* Edited by Gonser U, Osgood RM, Panish NB, Sakaki H. Berlin: Springer-Verlag; 1994. [Lotsch HKV (Series Editor): Materials Science, vol 19.]

4.   Masuhara H, De Schryver FC, Kitamura N, Tamai N (Eds): *Microchemistry: Spectroscopy and Chemistry in Small Domains.* Amsterdam: North Holland; 1994.

5.   Zimmerman FM, Ho W: **State resolved studies of photochemical
•   dynamics at surfaces.** *Surf Sci Rep* 1995, **22**:127–248.
This review gives a thorough overview of the state-of-the-art of laser based quantum state resolved studies on photochemical surface processes including studies on metal, semiconductor and insulator single crystal surfaces.

6.   Szymonski M, Postawa Z (Eds): **Desorption induced by electronic transitions, DIET VI.**In *Nucl Instrum Meth Phys Res (special issue)* 1995, **101**:1–230.

7.   Dai HL, Ho W (Eds): *Laser Spectroscopy and Photochemistry on*
••   *Metal Surfaces.* World Scientific Publishing Co: 1995: Parts I and II. [Cheuk-Yiu Ng (Series Editor): Adv Ser Phys Chem, vol 5.]
Two volumes of this excellent book contain 29 chapters written by established experimentalists and theoreticians on the field of laser spectroscopy and photochemistry on metal surfaces. The topics range from linear and nonlinear methods, real time spectroscopy on energy transfer dynamics, to investigations of laser-induced desorption and photochemistry. Each article starts with a basic and easy to read introduction followed by a summary of the main developments up to 1993.

8.   Hicks JM, Ho W, Dai H-L (Eds): *Laser Techniques for Surface*
•   *Science II, Proceedings of the SPIE's OE/Laser 95 Conference 1995; Washington.*Washington, DC: SPIE/the International Society of Optical Engineering; 1995.
These conference proceedings give a good insight into the most recent progress on topics such as ultrafast energy relaxation and surface femto-chemistry, desorption dynamics and photochemistry as well as adsorbate spectroscopy using linear and nonlinear optical methods in 1994 and 1995. New results on the growing field of liquids and biological surfaces are also presented.

9.   Miller RJD, Tully JC (Eds):**Surface reaction dynamics.** *Chem Phys*
•   *(special issue)* 1996, **205**:1–276. [Hochstrasser RM, Hofacker GL (Journal Editors): Chem Phys]
This special issue of *Chemical Physics* represents an update and synopsis of the current status of the field of surface reaction dynamics in 1996. Key issues treated include energy redistribution processes, barrier crossing dynamics focusing on the question of which vibrational modes of the adsorbate couple to the reaction coordinate, 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.

10.   Okiji A, Murata Y, Makoshi K, Kasai H (Eds): **International**
•   **Symposium on Dynamical Quantum Processes on Solid Surfaces DQPSS'95.** *Surf Sci (special issue)* 1996, **363**:1–456.
This special issue of *Surface Science* is recommended to anyone interested in progress on all aspects of dynamical quantum processes on solid surfaces within the years 1995 and 1996.

11.   Watanabe K, Sawabe K, Matsumoto Y: **Adsorbate-localized excitation in surface photochemistry: methane on Pt(111).** *Phys Rev Lett* 1996, **76**:1751–1754.

12.   Menzel D: **Thirty years of MGR: how it came about, and what**
••   **came of it.** *Nucl Instrum Meth Phys Res B* 1995, **101**:1–10.
This retrospective view by one of the fathers of the MGR model describing electronically stimulated desorption 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.

13.   Xin Q-S, Zhu X-Y: **Is localized collision responsible for O₂**
•   **photodesorption from Ag(110)?** *Surf Sci* 1996, **347**:346–354.
The important, but largely neglected, issue in surface reaction dynamics in chemisorption systems of the interaction between nascent reaction products and neighboring adsorbates is addressed. In the system presented 'hot' oxygen atoms are created during photodissociation of surface dioxygen. The atoms interact with co-adsorbed molecules aligned in the troughs on Ag(110) as on a one-dimensional 'billiard table' to cause photodesorption of molecular oxygen.

14.   Zenobi R: *Insitu* **analysis of surfaces and mixtures by laser desorption mass spectrometry.** *Int J Mass Spectrom Ion Proc* 1995, **145**:51–77.

15.   Jackson RC, Polanyi JC, Sjövall P: **Photodissociation dynamics**
•   **of (NO)₂ on LiF(001): characterization of vibrationally excited NO fragments.** *J Chem Phys* 1995, **102**:6308–6326.
The difficulty resulting from surface property changes in photochemistry of adsorbates is avoided in this work by studying the dissociation of a dimer, (NO)₂ on LiF(001). The desorbing NO molecules are detected state selectively. The high vibrational excitation of the desorbing NO is related to a de-excitation process after a direct excitation; the de-excitation process on the surface leaves one NO in the electronic ground state and the other NO in an electronically excited state with a large ON–NO distance. The energy distribution in the rotational and translational degrees of freedom are rationalized by assuming differing equilibrium geometries between the ground and excited state.

16.   Simpson CJSM, Griffiths PT, Curry JM, Towrie M: **The photolysis of NO dimers, adsorbed on an MgF₂ surface at 248 nm.** *Chem Phys Lett* 1996, **250**:342–348.

17.   Holbert VP, Garrett SJ, Stair PC, Weitz E: **The photochemistry**
•   **of CD₃I adsorbed on the TiO₂(110) surface.** *Surf Sci* 1996, **346**:189–205.
A very systematic investigation of the coverage dependence of the photochemsitry of CD₃I adsorbed on TiO₂(110) is presented using state-of-the-art quantum state resolved methods. Internal state and angular distributions of the desorbing methyl fragments and iodine atoms show differences to gas phase photochemistry and indicate the presence of multiple adsorption phases.

18.   Lu PH, Lasky PJ, Yang QY, Osgood RM Jr: **Dynamics of hot electron transfer in oriented methyl halides on GaAs(110).** *Chem Phys* 1996, **205**:143–158.

19.   Nessler W, Bornscheuer K-H, Hertel T, Hasselbrink E: **Internal**
•   **quantum state distributions of NH₃ photodesorbed from Cu(111) at 6.4 eV.** *Chem Phys* 1996, **205**:205–219.
Results on internal quantum state distributions after UV-laser induced desorption of ammonia from Cu(111) are discussed. As the spectroscopy of larger molecules is complex such studies are still quite rare. The data give new insight into energy transfer processes involving more than one molecular degree of freedom.

20.   Hertel T, Wolf M, Ertl G: **UV-stimulated desorption of ammonia**
•   **from Cu(111).** *J Chem Phys* 1995, **102**:3414–3430.
Measurements on the desorption efficiency of different isotopes are an important test of whether or not the observed laser-stimulated desorption can be described by a one-dimensional MGR mechanism; however, few such studies exist. Results on the system NH₃/Cu(111) are presented revealing a strong coverage and unusual high isotope dependence.

21.   Beauport I, Al-Shamery K, Freund H-J: **Rotational alignment in**
•   **the UV-laser induced desorption of CO from Cr₂O₃(0001).** *Chem Phys Lett* 1996, **256**:641-648.
This article treats stereodynamical aspects of the UV-laser stimulated desorption of CO from Cr₂O₃(0001). It demonstrates what we can learn from measurements of the alignment of angular momentum of desorbing molecules, of changes of adsorbate geometry during the excitation process, and of the involvement of other molecular degrees of freedom than the molecule–surface bond.

22.   Ishikawa K, Kanasaki J, Nakai Y, Itoh N: **Laser-induced bond**
•   **breaking of the adatoms of the Si(111)-7x7 surface.** *Surf Sci* 1996, **349**:L153–L158.
The authors present results on adatom desorption from Si(111)-7x7 using scanning tunneling microscopy. Such a combination of laser technology with atomic resolution probes on surfaces will stimulate significant developments within the field.

23.   Haight R: **Electron dynamics at surfaces.** *Surf Sci Rep* 1995,
•   **21**:275–325.
Experimental results on different aspects of electron dynamics at surfaces such as electron–electron scattering, electron–phonon scattering, diffusion, recombination and surface trapping are reviewed. The review gives a good insight into the main developments within this very quickly growing field.

24.   Knoesel E, Hertel T, Wolf M, Ertl G: **Femtosecond dynamics of**
•   **electronic excitations of adsorbates studied by two-photon photoemission pulse correlation: CO/Cu(111).** *Chem Phys Lett* 1995, **240**:409–416.
To follow the main step of laser induced desorption, the coupling of a hot charge carrier to an adsorbate, in real time is one of the most pressing topics today. This article presents the very first results for the system CO/Cu(111). As the process is fast, only the limits for the lifetime of the excited state can be obtained from two-photon-photoemission spectroscopy due to laser pulse width limitations.

25.   Cavanagh RR, Germer TA, Stephenson JC: **Ultrafast time-**
••   **resolved infrared probing of energy transfer at surfaces.** *Vib Spectrosc* 1995, **9**:77–83.
These established authors use picosecond and femtosecond IR techniques to characterize vibrational energy transfer rates after UV, visible and IR excitation of the systems CO/Pt(111) and CO/Cu(100). The differences of the systems are discussed in this very comprehensive paper and compared to theoretical model calculations.

26.   Culver JP, Li M, Sun Z-J, Hochstrasser RM, Yodh AG:
•   **Temperature-dependent coupling of low frequency adsorbate vibrations to metal substrate electrons.** *Chem Phys* 1996, **205**:159–166.
This interesting work presents studies on the vibrational energy transfer between the CO low frequency frustrated translation and metal substrate electrons of Cu(111) following femtosecond visible pulse excitation of the substrate. Emphasis is placed on the fluence dependence and the related temperature dependence of the process.

27.   Busch DG, Gao S, Pelak RA, Booth MF, Ho W: **Femtosecond**
•   **desorption dynamics probed by time-resolved velocity measurements.** *Phys Rev Lett* 1995, **75**:673–676.

Pump-probe techniques using femtosecond laser pulses are used by the authors to study the velocity distribution of O_2 photodesorbed from Pt(111) as a function of laser fluence and thus substrate electronic temperature.

28. Deliwala S, Finlay RJ, Goldman JR, Her JH, Mieher WD, Mazur E:
• **Surface femtochemistry of O_2 and CO on Pt(111).** *Chem Phys Letters* 1995, 242:617–622.
The nonlinear dependence of the desorption yield of O_2 and formation yield of CO_2 in the surface femtochemistry of O_2 and CO on Pt(111) is presented. A very systematic change of laser pulse duration from 80 fs to 3.6 ps and wavelength from 267 to 800 nm is the particular strength of the paper.

29. Nakatsuji H, Morita H, Nakai H, Murata Y, Fukutani K: **Theoretical**
• **study on the photostimulated desorption of CO from a Pt surface.** *J Chem Phys* 1996, 104:714–726.
One of the very first publications on electronically excited states relevant to photostimulated desorption treats the system CO adsorbed on a Pt surface. Calculations are performed by using the single excitation configuration interaction and the symmetry adapted cluster methods for a Pt_2–CO model cluster. Calculated excitation energy thresholds for CO, CO^+, and CO^* desorption explain the energy thresholds and the fluence dependencies of the incident laser in the photostimulated desorption experiments.

30. Klüner T, Freund H-J, Freitag J, Staemmler V: **Laser-induced**
•• **desorption of NO from NiO(100): ab initio calculations of potential surfaces for intermediate states.** *J Chem Phys* 1996, 104:10030–10040.
High quality *ab initio* complete active space self-consistent field and configuration interaction calculations are presented for the system NO/NiO(100) revealing the electronically excited states relevant to the desorption dynamics. The high ionicity of the transition metal oxide NiO(100) allows small clusters such as NiO_5^{8-} embedded in a Madelung potential to be used to obtain very reliable results.

31. Saalfrank P: **Photodesorption of neutrals from metal surfaces: a wave packet study.** *Chem Phys* 1995, 193:119–139.

32. Chakrabarti N, Balasubramanian V, Sathyamurthy N, Gadzuk JW: Photoinduced desorption in NO/Pt: a time-dependent quantum mechanical study. *Chem Phys Lett* 1995, 242:490–498.

33. Harris SM, Holloway S, Darling GR: **Hot electron mediated**
• **photodesorption: a time-dependent approach applied to NO/Pt(111).** *J Chem Phys* 1995, 102:8235–8248.
An innovative theoretical approach to the desorption dynamics of small molecules is presented in this paper for a system simulating NO desorption from Pt(111). In contrast to previous treatments excitation and relaxation steps are modeled together. The motion of the molecule and the hot electron generated in the substrate which resonates with an unoccupied molecular orbital of the adsorbate are treated on an equal footing.

34. Hintender M, Rebentrost F, Gerber RB, Kosloff R: **Molecular**
• **dynamics simulation of the photodissociation of adsorbed HCL on a MgO(001) surface.** *J Chem Phys* 1995, 102:578–584.
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 HCl/MgO(001) by the authors. A quantum effect is accounted for by taking the hydrogen coordinates and momenta in the initial state from a vibrational ground state wave function. The authors show that due to multiple collisions with the surface and the chlorine, the hydrogen can lose more than 3.5 eV of its 4.7 eV excess energy.

35. Brivio GP, Rossi ML, Torri M, Gortel ZW: **Time of flight spectra**
• **and chaotic dynamics in predesorption of physisorbed molecules.** *Phys Rev Lett* 1996, 76:3376–3379.
The authors present results on the vibrational predesorption of CO and CH_3F molecules physisorbed on NaCl(100) using a 2D model and classical

chaotic dynamics. The advantage of this method is that the time dependence of such an infrequent 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.

36. Dzegilenko FN, Herbst E: **Effect of coupling between frustrated translation and libration on the nonthermal desorption of physisorbed CO: three-dimensional quantum calculations.** *J Chem Phys* 1996, 104:6330–6337.

37. Stace AJ: **Can a molecule on a solid surface undergo a true (RRKM) unimolecular reaction?.** *Chem Phys* 1996, 205:153–158.

38. Brandbyge M, Hedegaard P, Heinz TF, Misewich JA, Newns DM:
•• **Electronically driven adsorbate excitation in femtosecond-pulse laser desorption.** *Phys Rev B: Condens Matter* 1995, 52:6042–6056.
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 to the adsorbate center-of-mass degree of freedom by a direct coupling mechanism is treated via an effective electronic friction and an associated fluctuating force.

39. Springer C, Head-Gordon M: **Simulations of the femtosecond**
•• **laser-induced desorption of CO from Cu(100) at 0.5 ML coverage.** *Chem Phys* 1996, 205:73–89.
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 frictional model in which the frictional kernel is evaluated by electronic structure calculations.

40. Ogawa S, Petek H: **Femtosecond dynamics of hot-electrons**
•• **at clean Cu(110) and Cu(100) surfaces.** In*Laser Techniques for Surface Science II, Proceedings of the SPIES OE/Laser 95 Conference: 1995; Washington;* Edited by Hicks JM, Ho W, Dai H-L. Washington, DC: SPIE; 1995:73–84.
The authors present state of the art measurements on the femtosecond dynamics of hot-electron relaxation in Cu(110) and Cu(100) using laser pulses <15 fs in two-photon time-resolved photoemission 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.

41. Germer TA, Stephenson JC, Heilweil EJ, Cavanagh RR:
•• **Picosecond time-resolved adsorbate response to substrate heating: spectroscopy and dynamics of CO/Cu(100).** *J Chem Phys* 1994, 101:1704–1716.
The authors present thorough time-resolved experiments on the infrared response of the CO stretch mode 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 translation 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 translation.

42. Tully JC, Gomez M, Head-Gordon M: **Electronic and phonon mechanisms of vibrational relaxation: CO on Cu(100).** *J Vac Sci Technol A* 1993, 11:1914–1920.