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# Electronically induced surface reactions: Evolution, concepts, and perspectives

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This is a personal account of the development of the title subject which is the broader field encompassing surface photochemistry. It describes the early times when the main interest centered on desorption induced by slow electrons, follows its evolution in experiment (use of synchrotron radiation and connections to electron spectroscopies; use of lasers) and mechanisms, and briefly mentions the many different subfields that have evolved. It discusses some practically important aspects and applications and ends with an account of an evolving new subfield, the application to photochemistry on nanoparticles. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4746799]

## I. INTRODUCTION

The coupling of molecules to surfaces induces changes in their properties which can lead to strongly modified reactivity. This is the basis of many surface effects, notably of heterogeneous catalysis with its potential of activity and selectivity in chemical reactions. It can be analysed by constructing potential energy surfaces (PESs) as a function of all degrees of freedom of the complete system, and follow the motion of representative points or wave packets on these PESs in the range of thermal excitations. Often one reaction coordinate only is considered, leading to potential energy curves.

Reactivity is also possible between electronically excited states of molecules which is the basis of photochemistry, since the necessary energy input is frequently obtained from photons. The representative set of PESs, usually crossing and interconnecting, now has to be extended to higher energies. These excited states will also be modified by coupling the molecules to a surface, leading to surface photochemistry. However, electronic excitations can also be induced by other means—mainly electron or ion impact—and these agents are often of practical importance. In fact the field started with excitations by electrons at a time when photon beams with low bandwidth and high intensity were not available for a broad spectral range as is the case now, and electron impact on surfaces obtained practical relevance. The processes occurring are largely the same (if we exclude the simultaneous direct energy transfer to atoms possible by ion collisions which we do not consider here). So it is preferable to use the more general term "Electronically induced surface chemistry" embracing all the ways to reach the higher energy PESs. Obviously the latter term encompasses the first one. In this essay both terms will be used, depending on the conditions used and the intended emphasis.

A general aspect of excited state chemistry is the fact that an electronic excitation takes the system or corresponding wave packet from the ground state to an excited state via a Franck-Condon transition, i.e., without change of nuclear coordinates. On the PES of the electronically excited state the wave packet will usually encounter a slope of the PES along one or more coordinates of the system, at the geometry of the ground state. If the system then evolves along the upper PES, energy is transferred from the electronic to the nuclear modes of the molecule. In addition to excitation of inner modes (rotations and vibrations) this can lead to photodissociation (more generally, electronically induced dissociation). The resulting fragments will often possess hyperthermal translational energy and internal excitations. If another partner is encountered, electronically induced reactions will ensue. Crossing PESs will add further complications and the consequent branching increases the possibilities of variable reaction paths.

All this will also happen on surfaces and will particularly concern adsorbates. Dissociation can now also happen to the adsorbate-substrate bond, specifically or in addition to other bonds; this will lead to electronically induced desorption of the adsorbate or fragments of it which, depending on the excitations involved, can be neutral or ionic. The surface-induced changes in electronically excited states of molecules include, in addition to more or less subtle changes within the adsorbed molecules, the possibility to exchange charge and energy between the molecules and the substrate via the latter's surface. This is particularly important on metal surfaces. In terms of PESs this means that the corresponding wave packet jumps from one PES to another; such processes can also be described by crossing of (suitably shifted) PESs, as will be shown below. These possibilities are now added to the energy transfer along sloping PESs mentioned above so the substrate can serve as source and sink of energy and charge. Specifically, the possibility of short-lived charged excited states of molecules coupled to a surface and their creation as well as their destruction by charge transfer from/to the substrate are of utmost importance for electronically induced surface reactions, particularly on metal surfaces. This will be discussed below. Throughout the paper the emphasis will be on concepts not formalism—there will not be a single equation. But there will be some personal judgements which not everybody might agree with.

**137**, 091702-1

This essay is structured as follows. Section II will give a brief historical account of the early development of the field, its roots in and its contributions to the development of surface science and vacuum technology which appears interesting in that it delineates the mutual influences in the evolution of these connected fields. Basic findings and the concepts derived from them will be sketched. Section III will collect a personally weighted compilation of important findings and developments over the decades, combined with an overview over applications to specific situations, for adsorbates on metal surfaces. Section IV will summarize briefly connected areas, such as electronically driven desorption from ionic insulators, from adsorbates on oxides, and from Van der Waals-bound systems (mono- and multilayers of rare gases and of molecular condensates). Section V will discuss some practical aspects and summarize examples of electronically induced surface reactions as a disturbance or an agent. As an example for recent developments an account of our findings for the additional aspects governing photochemistry on the surfaces of nanoparticles, as compared to surfaces of compact materials, will be given in Sec. VI.

## II. EARLY WORK AND EVOLUTION OF EXPERIMENTS AND CONCEPTS

Following early observations going back to 1918 (see the work cited in the reviews[1,2] and in Ref. 3) and concerning mainly the detection of ions from surfaces under electron bombardment, detailed research on electronically induced surface processes started in the early 1960s, around the same time modern surface science and its methodology took shape, and in a converging development from the same two roots: vacuum technology and surface chemistry. Vacuum technology as necessary for light bulbs and radio tubes had driven a large part of research on surface effects from the 1920s on, while the problems arising in connection with chemisorption and catalysis—which obviously needed improved methodology for basic understanding—arrived at similar questions. Their progress is intertwined as the preparation and investigation of well-defined surfaces, a necessary condition for detailed reliable studies of surfaces, needed ultrahigh vacuum (uhv) techniques to be developed; on the other hand an important prerequisite of reliable applications of uhv is the ability to measure the necessary low pressures; this met with difficulties which necessitated deeper understanding to be overcome. It is therefore not surprising that the investigation of electronically induced surface processes was tackled at the same time in the early 1960s from these two sides: by Redhead (R) in Ottawa from the vacuum technology side (who was prompted by the role such effects appeared to play in uhv ion gauges and mass spectrometer ion sources, influencing both total and partial pressure measurements[4]) and by Gomer and myself (MG) in Chicago (who approached these effects from the side of the chemical physics of surface interactions, using the only instrument that at this time could make sure that a well-defined surface was investigated, the field emission microscope (FEM).[5]) Accounts of the questions and problems behind these two lines of research, of the methods used—complementary also in that one (R) looked at the ionic

particles appearing in the gas phase and the other (MG) at what stayed on the surface, both deriving cross sections of the corresponding processes from the bombardment-induced signal or coverage decreases—and the findings and conclusions from them which nicely complemented each other, have been given in Refs. 3 and 6 and will not be repeated here. Most importantly, both[7,8] found that adsorbates could be removed from a surface by electrons with energies of the order of 100 eV, and that the corresponding cross sections were small compared to gas phase dissociation cross sections, and varied strongly. R (Ref. 7) also concluded that only a small part of the desorbed particles were ions (the species he detected directly), so that most must have desorbed as neutrals; and MG (Ref. 8) found in the FEM that besides desorption also dissociation, diffusion, and interconversion of adsorbates occurred. MG and R proposed essentially the same semi-classical two-step mechanism,[7,8] still known as "MGR,"[6] in which first a Franck-Condon quantum transition takes the system from the ground to the electronically excited state which then evolves classically along the excited state potential energy curve (only one dimension was considered and only repulsive excited states were considered then). During this evolution charge and energy can be transferred from the excited surface complex to the substrate which can be envisaged to occur at a curve crossing (see Fig. 1(a)) and, depending on the distance at which this happens, can transfer essentially the charge (leading to neutral desorption) or also sufficient energy to recapture the neutralized adsorbate in a bound state. The latter can either be the original ground state or a different stable adsorbate (e.g., a different binding state of the same adsorbate or a dissociated adsorbate). It was shown that there is a critical distance which separates processes leading to recapture from those leading to desorption (Fig. 1(b)). Menzel and Gomer[8] gave a quantitative description of these processes which, coupled with reasonable parameters, showed already at that early stage that the time scales of these processes had to lie in the low *fs* range or lower. We note already here that this mechanism (and similar semiclassical ones) is really at least a three-step process: a quantum excitation followed by classical evolution and a quantum de-excitation (which could be followed by further evolution on the ground state curve, a fourth step).

So the early work had shown that at least from adsorbates on metal surfaces mainly neutral particles were desorbed; that besides desorption other surface processes could be induced (i.e., that recapture can happen to a different ground state), and that mainly neutrals were desorbed from simple adsorbates on metals (even though it was much easier to detect the ions). In the following years more results using excitation by electrons were obtained, to which the group of Madey and Yates at the NBS contributed importantly.[1,2] Since in this period the main effect observed was desorption of adsorbates, the field was (and partly still is) labelled "electron stimulated desorption" (ESD) or somewhat later "desorption induced by electronic excitations" (DIET),[9] even though in many cases reactions other than desorption were observed as well. When the use of lasers made it possible to reach high intensities for visible or near UV light (for which, as mentioned, very low cross sections apply on metal surfaces) the term "surface
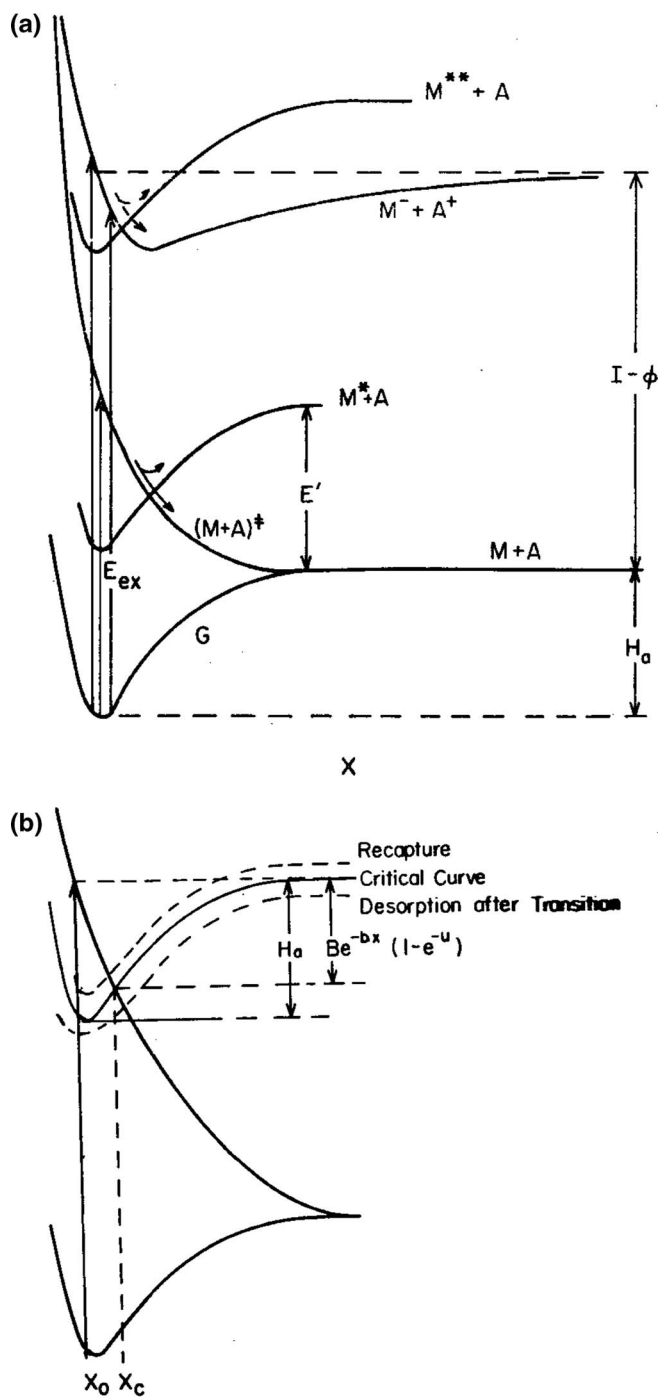
FIG. 1. (a) The MG picture of the MGR mechanism of electronically stimulated desorption. Electron collision with an adsorbate on a metal surface (G: bound ground state; M + A: separated system; x: coordinate of adsorbate bond) can take the system to a neutral antibonding state $(M + A)^*$ or an ionic state $M^- + A^+$ by a Franck-Condon transition. The systems evolving in the excited state along repulsive PE curves can be quenched to the adsorbate ground state at a variable distance by transferring energy and possibly charge to the substrate. These transitions can be modelled by crossing onto shifted ground state curves with excitation energy in the substrate, $M^*$ + A or $M^{**}$ + A. The particles escaping the recapture process can desorb as either neutral or ionic species. Starting on the ionic curve charge transfer can happen at a distance where the particle has accumulated enough kinetic energy to desorb as a neutral, leading to high neutral/ion ratios. (b) Sketch showing that a critical distance exists up to which quenching (i.e., crossing onto a suitably shifted ground state curve) leads to recapture while beyond it desorption occurs (for the case of an ionic excitation as a neutral). Reprinted with permission from J. Chem. Phys. **41**, 3311 (1964). Copyright 1964 American Institute of Physics.

photochemistry" became widely used,[10–12] discussing essentially the same processes.

A finding nicely corroborating the MGR mechanism was the discovery of a strong isotope effect which could be described quantitatively by the MG equations.[8] Here the first experiments were done by Madey and Yates,[13] followed by the observation of a more dramatic effect for adsorbed hydrogen.[14] The point here is that for 2 isotopes of the same adsorbate on the same surface, the PESs and the electronic excitations should be identical, while the evolution of the excited particle along the upper PE curve should depend on mass, with the heavier isotope moving more slowly and therefore being recaptured with higher probability. The MG equations[8] predicted a connection between the isotope effect for a certain mass ratio with the desorption probability which was well compatible with the results for O/W (Ref. 13) and H/W,[14] but drastically larger for the latter because of the low mass.

Madey and Yates also developed a method for obtaining geometry information from electronically induced ion desorption which they called ESDIAD (electron stimulated desorption ion angular distributions)[15] and which could be used to obtain adsorbate geometry information, in particular concerning adsorbate orientation and symmetry, at times where other methods like quantitative LEED and NEXAFS were not available. ESDIAD is still useful to follow certain aspects of thermal or electronically induced reactions in adsorbates. It may be noted that such measurements should be interpreted with possible artefacts in mind.[6, 16]

A basically different mechanism was proposed by Knotek and Feibelman[17] for ionic materials. Prompted by the observation that for oxides, ionic desorption thresholds (here for $O^+$) appeared at low-lying core levels (such as the Ti 3p in $TiO_2$, assumed to be of maximal valency even at the surface). If the ground state charge of the oxygen is $O^{2-}$, then 3 electrons have to be removed from it for desorption as $O^+$ to become possible which they argued can only happen by an interatomic Auger cascade transferring 3 electrons from the $O^{2-}$ to the Ti (assumed to be $Ti^{4+}$ in the ground state); the $O^+$ will then be ejected by the reversed Madelung potential. The highly publicized mechanism drew considerable new attention to these processes, and the emerging use of synchrotron radiation for core excitations further increased the attention. Today it appears questionable whether such processes are important—even for the prototype $TiO_2$ the surface layer may be not maximally valent but dominated by defects—and certainly the original suggestion that here is a means to selectively test the ionicity of a surface atom is incorrect. I will come back below (Sec. III) to core excitation-induced DIET and discuss an alternative view.

The work so far envisaged only repulsive excited states, so that the induced motion of atoms in the excited state would be *away* from the surface from the start. While the high excitation energies used made it probable that the excited state would be a positive ion state, already MG envisaged also the direct excitation of antibonding neutral adsorbate states; not long afterwards it was shown that such paths could indeed be induced by photon absorption in the near uv range,[18] albeit with very small probability. Antoniewicz[19] and Gadzuk[20]

proposed that there could be cases for which the effective radius of the excited state would be smaller than that of the ground state; in fact the ionisation of an adatom should have this characteristics. Then, the minimum of the excited state curve should be at smaller adsorbate-surface distance, and the initial acceleration would be *towards* the surface. A decay to the ground state by charge transfer would then bring the system onto the repulsive branch of the ground state curve which would possibly lead to its being kicked out. While the original case envisaged by Ref. 19 (excited state a positive ion) might not be frequently encountered, the general idea was important, and its most frequent realization is probably the so-called transient negative ion (TNI) mechanism.[12,21] This frequently invoked mechanism also breaks with another implicit assumption of MGR and maintained in the subsequent work: that the primary excitations take place in the adsorbate complex. Meanwhile it is known that especially at low excitation energies (below the ionization range, using visible and near uv light) such direct adsorbate excitations are quite improbable; it is much more likely that the primary absorption takes place in the substrate and creates excitations there which will mainly consist of hot electrons for a metal. Hot electrons of suitable energy can then tunnel into an adsorbate LUMO (Fig. 2(a)), creating a TNI whose charge will lead to image charge attraction. If the ground state adsorbate is weakly bound, this additional attraction will lead to an excited state curve with smaller distance from the surface, so that the TNI will start to move towards the surface (Fig. 2(b)). When the hot electron tunnels back into the bulk the system drops back onto the ground state curve but at too short distance, i.e., on the repulsive part of the curve, so that it is kicked out. Translational energy of the desorbing molecule stems mainly from this reflection (the acceleration in the TNI may contribute too); rotational energy can come from a torque in this configuration and from an "unfreezing" of the fixed angular axis in the ground state. If the reflection on the ground state curve is the main source of energy, translation and rotation should be positively correlated in the simplest impulsive approximation.[12] Vibrational excitation of the desorbate, on the other hand, would be caused by changes (usually a stretching, if the TNI has an electron in the LUMO of the adsorbate, since that is usually antibonding) of the internal molecular distances in the TNI state, which after return to the ground state would cause the desorbate to vibrate. The model in its simple form is sort of MGR backwards. We will come back to other actions of electrons originating from the substrate in Sec. IV.

All these arguments based on the basic semiclassical concepts have to be taken with a grain of salt. Zimmermann and Ho[12] have given a very detailed discussion of various ways semiclassical models such as the MGR and the TNI could be further specified for calculations. On the basis of the semiclassical nature of the models, with their separation of a quantum first step (i.e., a Franck-Condon excitation), and a classical evolution ended by a back-transition, many variations and improvements are possible.[12]

However, this semiclassical picture often cannot capture the real process. To stay with the TNI, its lifetime must be very short (of order 1 fs or less) since its formation and de-
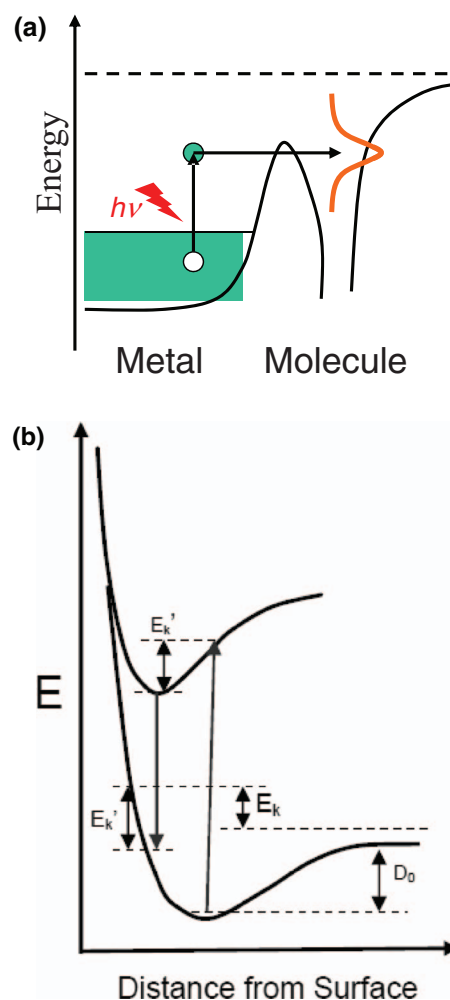


FIG. 2. (a) Sketch of the TNI process. Visible or near-uv photons are absorbed in the substrate, a metal, and create hot electrons. These can collide with the surface and, if their energy fits, tunnel into an unoccupied level of an adsorbate, where they will reside only briefly and then jump back. (b) Potential energy curves for the TNI sequence corresponding to an Antoniewicz process. The hot electron tunneling into the empty adsorbate level brings the system from the ground state to the more strongly bound TNI curve on which it starts to move towards the surface. When the electron jumps back into the substrate the system falls onto the ground state curve on the repulsive part and the adsorbate is kicked out.

struction (also important in MGR as the quenching step) are connected by microscopic reversibility, and the electron transfer to the adsorbate is known to be very fast from the strong quenching of primary charge in an adsorbate in this energy range, as well as the direct measurement of charge transfer times (see below). This easily explains why the cross sections of TNI-induced reactions are very small on metals. The small part desorbing must correspond to the tail of the lifetime distribution of the TNI. Even for these processes the time available for the quasi-classical evolution on the excited state curve should not be sufficient to allow a considerable shift of the adsorbate atoms (except for very low masses). In conceptual terms we appear to see the effect of a kick onto the adsorbate by the excitation, in a one-step inelastic scattering (excitation-deexcitation) process. The earliest attempt to treat such a situation was that of Brenig[22] who used an optical potential (in which the width of the state gives its lifetime which
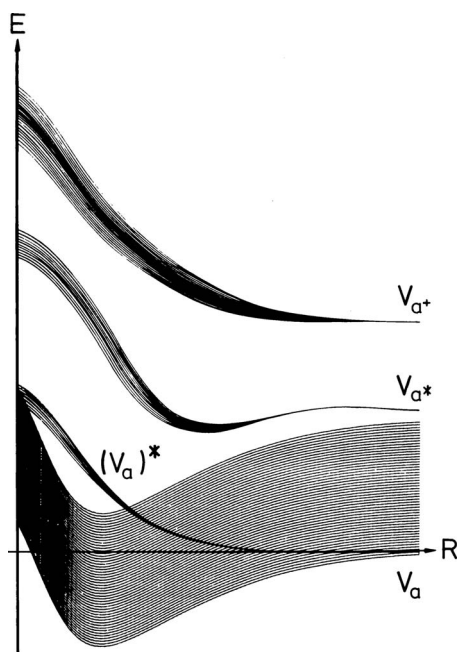
FIG. 3. Brenig's depiction of the MGR situation with an optical potential with varying width (corresponding to the state's lifetime) for the excited ($V_a^*$) or ionic ($V_a^+$) states and shifted ground state curves ($(V_a)^*$) (only a small number of these curves is shown; they extend semi-infinitely to higher energies) corresponding to the excitation having been transferred to the substrate. Reprinted with permission from W. Brenig, Z. Phys. B **23**, 361 (1976). Copyright 1982 Springer Science and Business Media.

varies with distance from the surface) and the distorted wave Born approximation to give a unified quantum representation of the quenching effect in ESD (Fig. 3). It corresponds to an action of the short lifetime on the wave packet in transition, so that it arrives distorted (in momentum space) on the excited state curve. Gortel[23] has shown that even with a totally flat excited state curve the excitation leads to momentum transfer to the adsorbate by wave packet (un)squeezing. Gadzuk[24] has discussed theoretical approaches which treat the DIET process as a resonant inelastic scattering event which allows some of these aspects to be taken into account in model calculations. Today the construction of PESs using DFT methods, and the analysis of wave packet motion on them in various ways extends the available theoretical treatments and allows to model more detailed results, such as state-resolved energy distributions in the desorbing particles (see Sec. III). A thorough review mainly addressing ultrafast processes, but also giving a more general discussion, has been given recently.[25]

## III. ADSORBATES ON METALS: FURTHER EXPERIMENTAL DEVELOPMENT AND SOME RESULTS

The rapid development of uhv technology and of the preparation of well-defined single crystal surfaces in the 1970s as well as the rapidly increasing number of surface-sensitive techniques (in particular electron spectroscopies[26]) with which the initial and final states of excitation could be characterized in detail gave a big boost to more in-depth in-

vestigations. Still the detection and analysis of particles leaving the surface after excitation remained an important tool. Another decisive development was that new photon sources became available and were increasingly used also in this field: synchrotron radiation (SR) and lasers. For improved understanding photons are preferable to electrons as excitation source because they make resonant excitations possible, while electrons can be considered as white light (up to their kinetic energy), leading to thresholds rather than absorption peaks. Furthermore, photon stimulation can utilize the light polarization for additional selection of the excitation. Therefore photons can pinpoint the primary interactions much better. SR delivers photons in the uv to x-ray region with ever increasing energy, energy resolution, and brightness. With SR it became possible to investigate in detail the energy dependences of a multitude of electronically induced processes and to connect them to corresponding spectroscopic results. Conversely, the high SR brightness makes it necessary to watch out even more for unwanted beam effects during spectroscopy and microscopy (see Sec. IV).

The broad application of SR for excitations in adsorbates at energies sufficient to excite ionic excitations and multiple excitations of valence and core electrons has yielded a large number of results which have expanded the understanding of the processes occurring in an adsorbate system after direct electronic excitation. In addition to the aspects mentioned above (desorption mainly of neutrals with a few percent positive ions in the valence ionisation range; other reactions such as dissociation, conversion, or diffusion also occurring; but cross sections much smaller than in the gas phase) other important findings were:

- For different binding states of the same adsorbate at the same surface the cross sections can be very different (up to factors of 10) which has already been seen in the first experiments[27] and confirmed many times. Usually (though not always; see next point) the more strongly adsorbed species has the lower cross section.
- The cross sections for desorption by valence excitations are often highest for low coverages and become smaller with increasing coverage[28] (extreme example: H/W(100) where the low coverage cross section is $10^3$ times higher than that at full coverage;[29] see Fig. 4). This has been explained by lateral delocalisation of the excitation or intrinsically delocalised excitations if the adsorbate forms two-dimensional (2D) bands. Indeed a connection between desorption cross section and 2D band width has been found.[28] The cross sections are particularly high for adsorbates at defect sites.[30] This can lead to the situation that the predominant parts of desorbing particles come from a small percentage of the coverage. Obviously, ESD is a very poor quantitative probe.
- The cross sections increase for multiple valence excitations and even more for core excitations[17, 31] and core-valence multiple excitations.[32] This selective enhancement of low probability excitations has made it possible to detect such multiple excitations in
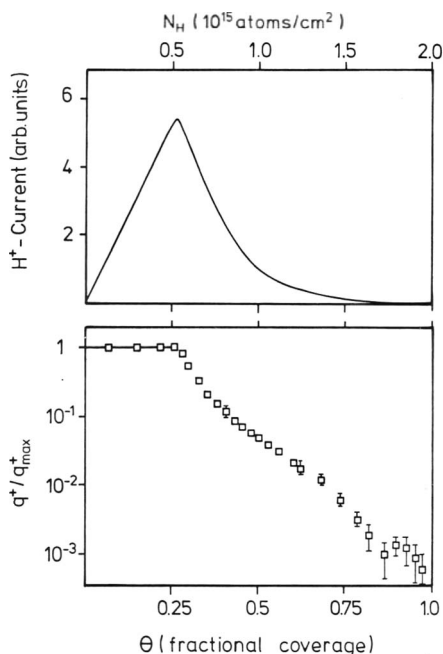
FIG. 4. Top: The electron stimulated $H^+$ signal from H/W(100) as a function of coverage. Bottom: The cross section variation with coverage, normalized to the high cross section at low coverage. Data from Ref. 29.

adsorbates before they were seen in free molecules, partly through detection of singly and multiply ionized desorbing species[32] (see Fig. 5).

We have discussed these aspects under the heading localisation vs. delocalisation.[6] The argument is that in order to
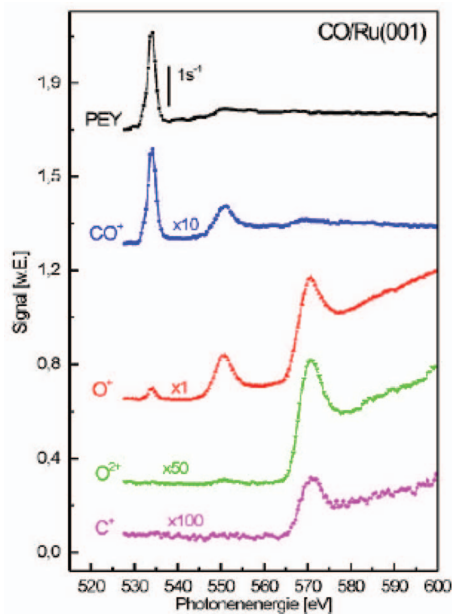


FIG. 5. Core level excited photodesorption of the ions given, from CO/Ru(001) at and above the O 1s excitation, using mainly s-polarized light to couple to excitations with overall $\pi$ symmetry. The top spectrum (PEY, partial electron yield) gives the photon absorption. The peak at ~532 eV is the single excitation from the O 1s to the CO $2\pi^*$ LUMO; it is strong in $CO^+$, weak in $O^+$, and absent in the other ions; strong peaks for them can be connected to multiple core-valence excitations (see Ref. 32 for details). Data from Ref. 32.

lead to bond breaking, an excitation has to stay localised on an individual bond for sufficiently long time to transfer the required energy to the few atoms involved. Any effect which decreases the localisation time (strong surface bond leading to rapid delocalisation into the bulk; delocalisation to neighbor adsorbates, e.g., within a surface band, in particular at high coverage) will decrease the cross section. Any effect which increases the localised lifetime (weaker coupling to the surface; low coverage; zero-dimensional adsorbate at a defect; intrinsically localised excitation such as a core excitation which can be further enhanced by correlation in multiple excitations) will increase the cross section. This tendency can also be seen in isolated larger molecules and is consistent with the finding that for organic molecules those with $\pi$-bonds are much more stable against electronically induced dissociation than those with $\sigma$-bonds: in the former the delocalised excitation is less likely to localise on an individual bond before the excitation is converted into other modes (mostly vibrations in molecules; electron-hole pairs at metal surfaces) than in the latter (see also Sec. IV in this connection).

As to the effect of multiple excitations, it should be remembered that correlation—which couples these multiple excitations—leads to localisation of the excitation by its Coulomb interaction (Cini-Sawatzki effect[33] known from Auger spectroscopy: atomic *vs.* band spectra). A conceptual explanation is that in a doubly ionized atom the two charges will stay apart as much as possible, so that overlap of both charge distributions with the same neighbor is unlikely. The alternative—the two holes jumping simultaneously to different neighbors—is energetically impossible if the Coulomb interaction is larger than the electronic bandwidth of the system of neighbors which would have to accept the two holes. This effect is even stronger for more than two charges because of increasing correlation, so that it becomes understandable that the more complex the multiple excitation, the larger the cross section. This can overcompensate the low excitation probabilities of such excitations, so that they become selectively observable in the desorbing fragments. It should be noted that another effect plays an important role as well in increasing the signal (and the final state energy of desorbed molecules; see below) from multiple excitations: Higher excitations will usually possess higher slopes of the respective PES, so that less localisation time is necessary to transfer sufficient energy for bond breaking. We have shown that these two aspects can explain the selective bond breaking by core electron excitations observed for adsorbed molecular nitrogen on Ru(001) but not on Ni(111).[34]

As to lasers, their use became more and more general in the low energy range, with their high intensity overcompensating the low desorption probabilities existing at least for adsorbates on metal and semiconductor surfaces. Today we know that at low excitation energies (visible to near UV photons or corresponding electron energies, i.e., below ionization energies) most electronically induced processes proceed via substrate-mediated mechanisms such as TNI (see Sec. II). With lasers as excitation sources, the realm of nonlinear mechanisms and ultrashort time resolution became accessible which has contributed importantly to the understanding of photochemistry at surfaces and of the time scales of
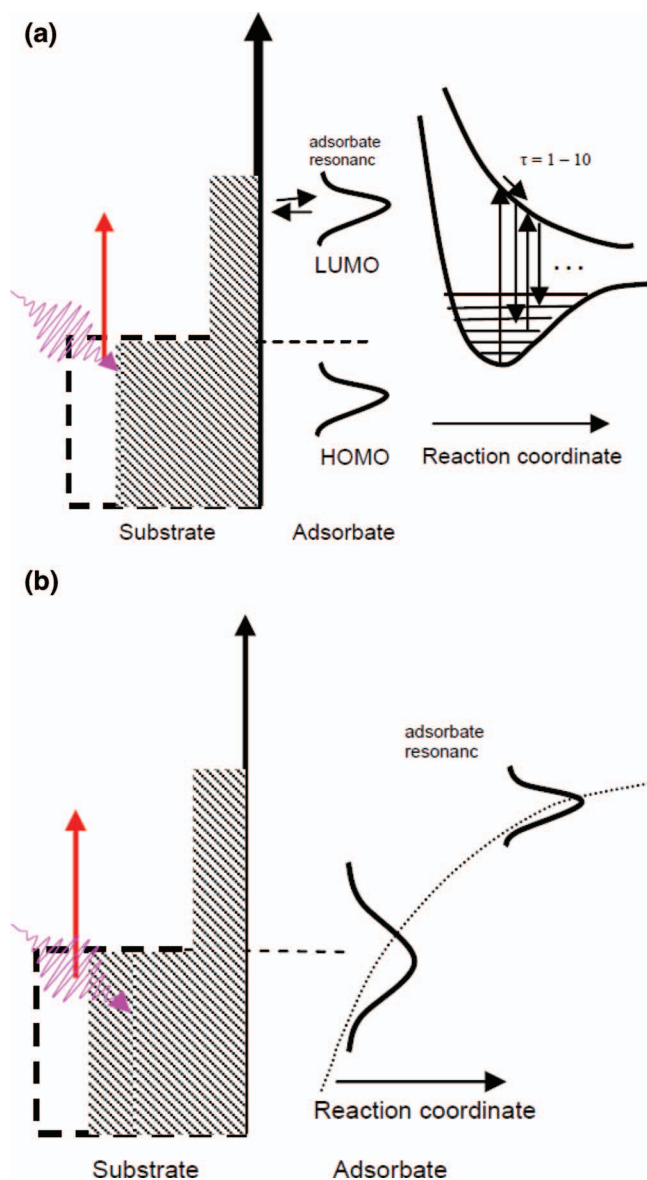
FIG. 6. (a) Sketch of the DIMET process. At high temporal photon density the effect of a first excitation which does not suffice to lead to desorption can still be present in an adsorbate vibration, so that the system can be pumped to desorption by several accumulating excitations. (b) Sketch of the frictional pump-up by many small excitations connected with charge fluctuations between adsorbate and substrate close to the Fermi level.

surface excitations in general. Mechanisms of nonlinear excitation such as DIMET (desorption induced by multiple electronic transitions)[24,35,36] and frictional excitation[24,36] assume that in cases where the probability of a single excitation leading to desorption is very small, the overall probability can be nonlinearly increased if several excitations happen in a sufficiently short time, so that the effect of a single excitation is still contained in the excited adsorbate when the next one occurs (Fig. 6). Conceptually, the two mechanisms differ in whether there are a few large (DIMET) or many small (friction) excitations accumulating in the adsorbate complex; they can be treated as extreme cases in a unified model.[24,35,36] Naively one would assume that it is sufficient for the energy accumulation to occur within the lifetime of vibrational exci-

tations of an adsorbate on a metal which are of the order of some ps. This would mean that the multiple excitations could be accumulated in the adsorbate incoherently. However, there are results which suggest that the acceptable temporal spacing of individual excitations is shorter, possibly even much shorter[37] (in the given reference the laser pulse length limited the time resolution). This means that the multiple excitations have to be superimposed coherently which makes sense in particular for the friction model. One variant for a particular class of systems will be mentioned in Sec. VI. Other essays in this special issue may discuss such questions in detail; therefore I will not expand on it here. Suffice it to say that the early estimates[8] of very short lifetimes (some fs or even lower) of electronically excited states on metal surfaces have been directly corroborated even though not all researchers agree on the numbers.

While this aspect of excitation lifetimes, being a sideline for our subject, cannot be discussed in detail here, it should be pointed out that methods exist to directly measure lifetimes of electronic excitations—say, of an electron in an adsorbate LUMO (i.e., a TNI) or a hole in a HOMO of an adsorbate. It is interesting to note that a method utilising core hole life times as an internal clock[38] generally arrives at times in the low fs range for physisorbed atoms and down to fractions of a fs for chemisorbed systems[39] while laser pump-probe methods[40] arrive at somewhat longer lifetimes. I cannot offer an explanation for that discrepancy and am not aware of one. We may hope that the recently developed methods of attosecond spectroscopy[41] which are rapidly evolving and are beginning to be applied to surface systems,[42] will resolve the open questions.

Laser methods such as resonance-enhanced multiphoton ionization (REMPI) and laser-induced fluorescence (LIF) applied to the detailed characterization of desorbing particles have also greatly enhanced our understanding of the dynamics of evolution of the wave packets on the coupled excited and ground state PESs by supplying information, in addition to translational energy distributions of neutral desorbates and their angular dependences (which can be obtained by time-of-flight methods), also on rotational and vibrational energy distributions[12,25,43] so successful in the analysis of the dynamics of molecules scattered on or thermally desorbed from surfaces. The dramatic advance of theoretical calculations of PESs and of motion on them that has come about by the development of density functional theory and wave packet methods, has made it possible to model such details (see Sec. II). Comparison of experimental and calculational results then can show whether the underlying concepts are correct, and can supply parameters which are not directly accessible.[12,25,43] As an example from our own work, for CO desorbed from Ru(001) by electron impact of sufficient energy to cause multiple valence excitations (stressing again the influences of correlation-induced localisation and high repulsiveness of such states), extremely high, inverted vibrational excitations—actually all the way of to dissociation of CO—have been found by REMPI.[44] An advanced theoretical treatment, using DFT calculations of PESs coupled with wave packet methods has been able to model these results.[45]

## IV. ELECTRONICALLY INDUCED PROCESSES ON NON-METALS

In an attempt at completeness, this section will summarize quite briefly a number of areas which are connected to our topic. The points given should enable the interested reader to enter the mentioned fields for more detailed information.

As for surface science in general DIET research addressed mainly metal surfaces for a long time. In the last two decades the study of well-defined insulator surfaces, in particular of oxides, has become a hot area, and the research of photochemistry on them has followed suit. For adsorbates on insulators bonding in the ground state, as well as interactions in the excited state including charge and energy transfer, are more localized, so that generally much higher cross sections are found compared to the same adsorbates on metal surfaces, even at low excitation energies; this is understandable from the missing fast transport of excitations into the bulk. This eases the theoretical treatment somewhat; also the researchers entering this research found a well-developed field experimentally and theoretically, so that the treatments were quite advanced from the start. This can be seen, e.g., from the review Ref. 46 which not only gives an overview over theoretical treatments of laser photodesorption from adsorbates on oxide surfaces but also lists a large number of experimental papers.

The history goes back further for condensates of atoms and molecules, and for surfaces of bulk insulators. Here bulk excitations can be created which can migrate to the surface and become effective there, somewhat like hot electrons inside a metal (see above). If an excited state cannot be easily quenched in the bulk its lifetime will approach that for the isolated particles. For insulator surfaces many processes in the bulk involving specific transportable excitations (excitons, color centers, etc.) have been identified to contribute to the desorption of ions and neutrals. The bulk can act as collector of excitations which due to the large band gap are long lived, can migrate to the surface and desorb surface species. Electronic ablation can be extremely efficient, in particular for primary electrons, since they need not match the specific excitation energies and can produce copious secondary electrons, thus multiplying the number of excitations. This is the case for alkali halides where efficient desorption of halogen and alkali atoms and accumulation of alkali metal (at low temperatures) on the surface is observed[47] which can be explained by a mechanism proposed in the 1960s for exciton creation and F-center trapping.[48] The desorption of alkali cations has been assigned to electron collisions above the surface rather than a Knotek-Feibelman sequence.[49]

Specific surface and bulk excitations also govern desorption of atoms from mono- and multilayers of rare gases. The strongest excitations in rare gas solids are the excitons which can easily migrate and which are less energetic at the surface.[50] Furthermore, in these Van der Waals-bound systems the formation of chemical bonds in the excited (neutral or ionic) state can occur. In monolayers of the rare gas X, e.g., on a metal surface, the neutral excited $X^*$ as well as the ionic $X^+$ can interact with the surface chemically to form an excimeric or ionimeric adsorbate with considerably in-
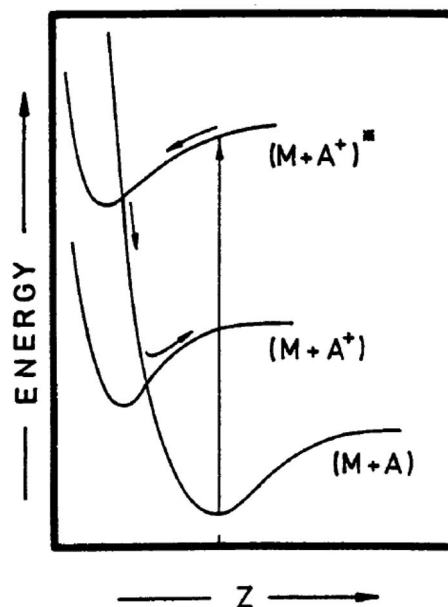


FIG. 7. Sketch of the excimer/ionimer desorption mechanism of rare gases in monolayers and condensates. An excited or ionized adatom A can form a chemical bond with a neighboring atom or the surface M. The system evolves towards shorter bondlength during the lifetime of the quasi-molecule. When the excitation or charge are removed (indicated by curve crossing) the system returns to the ground state at too short distance and flies apart. From the monolayer desorption of neutral atoms occur for a single excitation; a higher excitation is needed to lead to desorbing ions. Reprinted with permission from P. Feulner and D. Menzel, *Laser Spectroscopy and Photochemistry on Metal Surfaces*, edited by H. L. Dai and W. Ho (World Scientific, Singapore, 1995), p. 627. Copyright 1995 World Scientific Publishing Co.

creased bond strength (and decreased bond length) to the surface (Fig. 7), compared to the essentially physisorbed ground state.[51] This is another example of an Antoniewicz-like process which leads to an evolution formally similar to that of a TNI. In rare gas multilayers or crystals a related scenario can occur: an excimer or ionimer locally formed with a ground state neighbor leads to an evolution towards decreased bond length; when the excited state decays (by photon emission for the excimer, and electron capture for the ionimer) the pair drops back onto the repulsive branch of the ground state curve, and the momentum kick imparted onto the neighbors can be transmitted through the solid by a collision cascade and kick out a ground state atom at the surface. Another scenario, cavity ejection (Fig. 8), is possible for negative electron affinity solids (Ne and Ar): an exciton produced by photon absorption or electron collision leads to a local expansion of the electron cloud. If the location is not too far from the surface a gradient of energy towards the surface is imposed, leading to directed diffusion of the exciton (or just the excitonic state) and self-trapping at the surface. The resulting asymmetric forces lead to expulsion of an electronically excited $X^*$ atom which can be detected via the photon emitted in its decay in the gas phase.[52]

Electronic excitation of thin films of condensed molecules can lead to molecular dissociation (possibly followed by reactions with neighbor molecules) via all paths known for free molecules, such as dissociative attachment
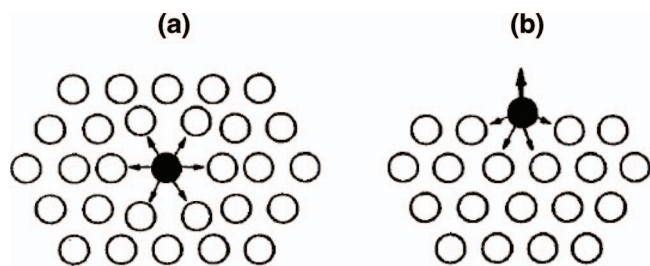
FIG. 8. Sketch of the cavity ejection mechanism for desorption of electronically excited atoms from condensed light rare gases. (a) Self-trapping of atomic excitons in the bulk leads to cavity formation. (b) After diffusing to the surface the asymmetric repulsion ejects an excited atom. Reprinted with permission from P. Feulner and D. Menzel, *Laser Spectroscopy and Photochemistry on Metal Surfaces*, edited by H. L. Dai and W. Ho (World Scientific, Singapore, 1995), p. 627. Copyright 1995 World Scientific Publishing Co.

(DA), bipolar dissociation into cation-anion pairs, and dissociative ionisation, depending on the kind and energy of the excitation used. A large literature exists on the details of these processes and their interpretation and use[53] which can only be mentioned here briefly. Suffice it to say that DA of molecules appears to be a very important path for radiation damage, e.g., of aqueous systems and of genetic material, in the production of molecules in space and in primordial systems. This will be revisited in Sec. V.

## V. PRACTICAL ASPECTS: WANTED AND UNWANTED EFFECTS

Electronic excitations can cause desired as well as unwelcome, disturbing effects. Their use in technology is wide—suffice it to mention the structuring of resins in the production of semiconductor devices. The sensitivity of large organic molecules to radiation-induced reactions like cross-linking or fragmentation for the creation of positive as well as negative structures on a surface is important for these processes. Photocatalysis and Electro-Photocatalysis are broad fields which apply radiation-induced reactions in a positive sense. In fact much of the research described above is being motivated by improving the basic understanding for designing better processes in these ranges.

There is a wide range of electronically induced effects which are detrimental to the intended goal or outright damaging. All kinds of radiation damage belong in this class, and it has been argued[54] that a major source of damage to biological structures, even caused by relatively high energy electrons and photons, is caused by slow electrons produced under these conditions. This makes it important to consider these processes.

Slow electrons coming from the substrate or the interior of a condensate can cause reactivity in the excited state via transient attachment to a surface species. This is the basis of the TNI mechanism discussed in Sec. II. It is also the basis of the radiation damage via dissociative attachment (DA) mentioned above. Damage to DNA and other biological molecules can be largely due to DA caused by slow electrons.[54] It is important to realize that in order to activate these mechanisms it is not necessary to start with fittingly low energy electrons.

In any solid electrons can lose energy by inelastic scattering, so even when we start with electrons or photons of much higher energies the secondary electrons scattering through the substrate will have a broad energy distribution and eventually reach any energy necessary for dissociative ionization, for creation of excitons or polarons, or for dissociative attachment, be it via TNI at metal surfaces or via negative ion resonances in molecules. On the other hand, as already mentioned, large organic molecules with (preferably extended) $\pi$-electron systems have a protective function against radiation damage, as the delocalization of excitation over an extended system prevents its concentration on a single bond, so that even in a molecular system the excitation can be drained into vibrations/phonons. This may contribute to the particular capacity of DNA to resist photodamage.[56] In a model system, perfluorinated Cu-phthalocyanine, where damage-resistant behavior was found, we have argued similarly.[57]

This effect of secondary electrons which can lead to desorption via slow or hot electrons is often observed for higher energy photons and electrons for which primary excitations have lower cross sections. The abundant production of slow secondary electrons with wide energy distributions can here lead to very efficient electronically induced processes, be it via TNI formation for low energies or via antibonding or ionic excitations by electron impact from within. These processes are particularly important for practical situations such as electron spectroscopy (usually with primary VUV to SX photons) or electron microscopy[55] where electronically induced surface reactions are a major problem because they can change or destroy the surface species to be investigated. This is of enhanced relevance when very high brightness photon sources such as free electron lasers are used. The direct excitation of adsorbate complexes for photon absorption is observable, despite this background of reactions induced by secondary electrons (often called XESD, x-ray induced electron stimulated desorption), by selecting resonant valence or core excitations or their multiple excitations. The use of narrow band SR makes the separation easier, even though a peak of a desorption signal, observed at a certain photon energy corresponding to a definite excitation of the adsorbate or surface species, does not mean that this is not caused by XESD: The observed peak in the signal could simply stem from the high total absorption and still be caused by XESD (see Ref. 58 for a discussion for water mono-and multilayers). A good indicator for the absence of XESD in, e.g., core excitation-induced photodesorption such as those shown above (Fig. 5) is the absence or weakness of signal at substrate core level resonances.[32]

Water actually is a particularly endangered species. The cross sections for dissociation by low energy electrons are very high [see the discussion in Ref. 59), so that one has to be very cautious to accept spectroscopic evidence of dissociation of adsorbed water—it could easily be caused by the spectroscopic investigation. The classical example is the state of adsorbed water ($H_2O$ as well as $D_2O$) on the close-packed Ru(001) surface. A vivid controversy[59,60] ran for quite a while before it was clear that indeed molecular layers can be formed for both isotopes but can easily be dissociated under the conditions of SR spectroscopy as well as in LEED investigations, with $H_2O$ being more easily destroyed than $D_2O$.

# VI. PHOTOCHEMISTRY AT NANOPARTICLE SURFACES

The discussion so far has concerned the electronically induced reactions on well-defined single crystal surfaces in the surface science sense. A very interesting and practically important type of substrates are nanoparticles in the size range of up to about 10 nm, usually of metals (MNPs, metal nanoparticles) supported on more or less inert substrates (usually oxides). The utmost importance of thermal reactions on such systems for heterogeneous catalysis need not be emphasized. Investigations of model systems of this type have improved the understanding of practical catalysis and have pinpointed many important properties of such systems.[61]

It is a valid and interesting question whether on such systems also reactions of electronically excited molecules will show properties characteristically different from those of the surfaces of bulk crystals which have been the focus of this essay so far. An examination of what is known about the excitations of MNPs has suggested that indeed definite changes of photochemistry (this term is used here because we are only concerned with photon excitation in the visible to near-uv range) can be expected compared to compact materials.[62] While many minor changes can be pinpointed, the two most important changes to be expected concern new characteristic excitations—in particular the strong Mie or particle plasmons[63]—and the fact that excitations cannot easily disperse into the bulk as on compact materials—an effect which can be called "excitation confinement". In the past 7 years a group at the Fritz-Haber-Institut in Berlin has investigated in detail one test reaction system, directly comparing NPs and bulk material. We believe that the findings are quite typical for what can be expected generally. In the following a short summary of the experiments, their results, and the conclusions drawn will be given.

Since one of the expected effects was the influence of Mie plasmons the material chosen was silver. The deposition of silver nanoparticles (Ag NPs) on ultrathin alumina films (on AlNi alloy surfaces) has been studied and their properties have been characterized in detail in Berlin.[61] The preparation of narrowly defined particle sizes in the range 2–10 nm is possible. A strong plasmon mode at ~3.5 eV (polarized perpendicular to the surface; the expected lower energy parallel mode is screened by the close-by metal substrate) has been observed and characterized by photon STM[64] (Fig. 9) and by two-photon photoemission (2PPE).[65] The thin alumina film decouples the Ag NPs quite efficiently electronically from the metal substrate without leading to charge-up; this should lead to excitation confinement. NO was chosen as adsorbate because of the ease of its state-selective detection which makes it a frequent test adsorbate. On silver, however, its adsorption is more complex than usually observed on (transition) metal surfaces. Its weak interaction with the noble metal leads to necessary adsorption temperatures below 80 K; in this range NO dimers are formed on the surface. On Ag(111) the resulting adsorption layers have been studied in detail[66] including their photochemistry;[67] these extensive studies provided a good basis for our experiments. Because of the dimer formation the photochemical reaction channels
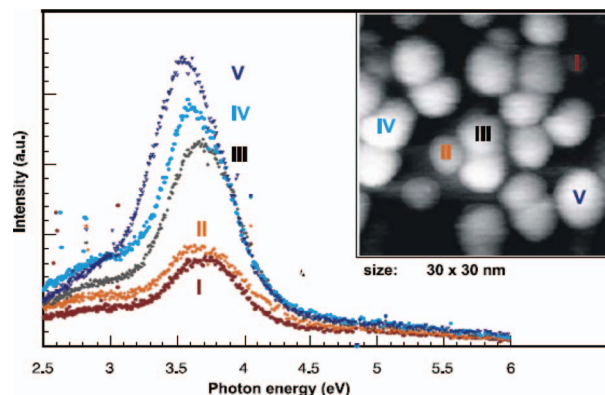


FIG. 9. Inset: Ag NPs on thin alumina films as seen in the photon STM, displaying NPs of varying sizes (I–IV). Main figure: The photon emission spectra recorded by electron excitation of the NPs I–IV, showing the plasmon energy range and width, and the variation with size. Reprinted with permission from N. Nilius, N. Ernst, and H.-J. Freund, Phys. Rev. Lett. **84**, 3994 (2000). Copyright 2000 American Physical Society.

are more complex than on transition metals. Besides breaking of the ON-NO bond and the bond to the surface simultaneously which leads to NO desorption into the gas phase and leaves some monomeric NO on the surface, the dimers can also react to $N_2O + O$ which stay on the surface ($N_2O$ can be detected by subsequent thermal desorption; adsorbed O leads to a stronger bond of the NO monomer which desorbs thermally at much higher temperature and has a much smaller photoreaction cross section than the dimer). Even the photodesorption of (extremely fast) $N_2$ molecules has been observed under certain conditions.[68] Here we concentrate on NO desorption, the strongest photoinduced channel. Besides measuring yields and desorption cross sections, the energy distributions over the translational[69] and internal modes (rotation, vibration)[70] of the desorbing NO have been recorded, all these for varied photon energy and polarization, particle size, and laser pulse duration. Direct comparison to Ag(111) in the same experimental system and with the same methods has been made in all respects.

We found the following main results:

(1)  The photochemical mechanism is believed to involve TNI states on flat and rough Ag surfaces.[12,21] This is also (almost always; see below) the case for Ag NPs as corroborated by our detailed characterizations of the desorbing NO (Ref. 69; see (5) below). That is, a hot electron of energy in the TNI range (i.e., that of the adsorbate LUMO) which is excited in an NP by the absorbed light tunnels from the NP into an adsorbed $(NO)_2$. The N-N and N-O bonds are weakened, and the bond to the surface is strengthened by the charge—image charge interaction. The corresponding wave packet is put onto the excited state PES in an area with potential gradients in all dimensions. When the electron jumps back into the NP after a very short residence time the adsorbate molecule has evolved sufficiently along the gradients to lead to breaking of the N-N and the NO-Ag bonds and to translational, rotational, and vibrational excitation of the desorbing NO.
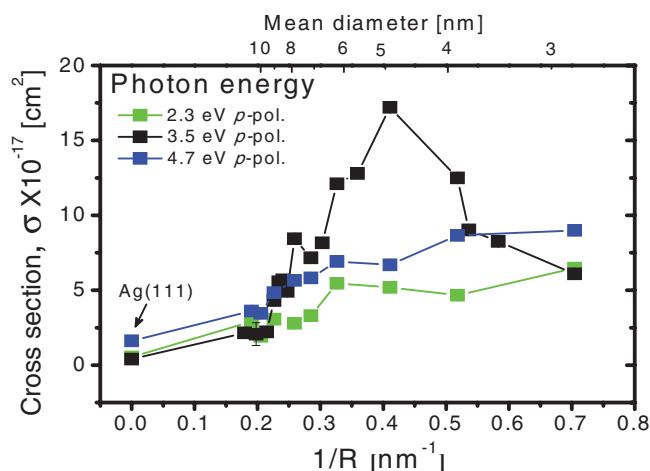
FIG. 10. Variation of desorption cross sections, $\sigma$, of NO from $(NO)_2$ mono-layers on Ag NPs as a function of mean particle size (top abscissa), for the 3 photon energies given (bottom abscissa: inverse NP radius). For 2.3 and 4.7 eV (outside the plasmon resonance) the cross section roughly scales with $1/R$, i.e., the surface/volume ratio. At ~3.5 eV (p-pol.) the plasmon is excited, leading to much stronger enhancement and a clear maximum at a certain particle size. Reprinted with permission from D. Mulugeta, K. H. Kim, K. Watanabe, D. Menzel, and H.-J. Freund, Phys. Rev. Lett. **107**, 146103 (2008). Copyright 2008 American Physical Society.

(2) The cross section, $\sigma$, for NO desorption from $(NO)_2$ monolayers on Ag NPs is indeed strongly enhanced for excitations in the plasmon resonance known to be around 3.5 eV, weakly dependent on particle size:[64, 65] a factor 40 (depending on NP size; see (4) below) relative to Ag(111) has been found.[69] This is understandable from the fact that the antenna effect of plasmons concentrates more photons into the NPs. Since most or all plasmons (depending on the NP size[63, 69]) decay into electron-hole pairs by Landau damping[63] the number of hot electrons able to induce the TNI effect will increase correspondingly.

(3) An enhancement of $\sigma$ exists also off the plasmon resonance, albeit weaker (factors 2–3), which we assign to confinement of hot electrons in the Ag NP which here are produced directly by photon absorption.

(4) The cross section enhancement depends on NP size (Fig. 10 (Ref. 69)). Generally—i.e., off the plasmon resonance—it increases with decreasing NP size (diameter d) which is understandable by confinement of the primary hot electrons in the NP ($\sigma \sim 1/d \sim S/V$, the surface/volume ratio). For plasmon excitation a strong maximum of $\sigma$ at a certain NP size (here at d ~ 5 nm) is superimposed. It is explained by two counteracting influences: on the one hand the probability of the decay of plasmons into hot electrons (by Landau damping) increases with decreasing NP size against the competing radiative decay;[63] on the other hand the total number of photons collected decreases with the number of atoms in the particle.[69, 70]

(5) On the other hand the dynamics of the bond dissociations and internal mode excitations, dictated by the motion of the representative wave packet on the potential energy surfaces of ground and excited states for the var-

ious evolving molecular entities, is found to be (almost) always the same. This is concluded from the fact that the final state of the desorbing NO stays constant: all energy distributions, translational, rotational, and vibrational, as well as their correlations, are identical despite the strong variations of cross sections.[69, 70] These characteristics are well compatible with the proposed TNI mechanism (see (1)). The only exception to this constancy of mechanism is found for excitation with the highest photon energy used (4.7 eV) and the smallest NPs (d < 4 nm), where the mean translational energy of NO was considerably enhanced—in fact a new much faster component was found in addition to the normal one.[69, 70] We have explained this new path by excitation of a transient *positive* ion of the NO dimer accessible at an excitation energy sufficient to produce holes in the Ag d-band or direct excitations from a filled adsorbate state to empty states of the NP. That this path becomes observable only for very small NPs is due to the fact that its contribution is proportional to the surface area while the TNI contribution goes down with the volume.[69, 70]

(6) All these results were obtained with nanosecond lasers at fluences which lead to linear behavior of the photochemical yield with fluence, i.e., the determined cross sections are independent of fluence. This shows that the excitations do not interact, even when they are confined in an NP—there is at most one excitation per ps and NP—which must be due to their short lifetime. Very different behavior is found with femtosecond (~100 fs) laser pulses of the same or even smaller fluences, for which the photons of a pulse arrive in a much shorter time so that the spatio-temporal photon density is increased by at least a factor $10^4$.[71] Here the cross section is found to be considerably enhanced and to increase with fluence; i.e., the yield has nonlinear fluence dependence. Two-pulse measurements, in which one pulse is split into two which are then delayed with respect to each other, show that the memory of the system is confined to the time of overlapping pulses. So there is a very short-lived interaction of hot electrons which causes the nonlinearity. We have explained this by a re-pumping of hot electrons within the same pulse, made possible by the confinement in the NP.[71] This is a different nonlinear enhancement from those discussed previously for photodesorption from compact substrates, the DIMET and the friction mechanisms;[35–37] it is only possible on NPs. However, despite this dramatic change of reactivity again the mechanism of desorption, as indicated by the NO final state energies, was found to be unchanged.

To summarize this section, we find that MNPs can induce large increases of photochemical cross sections compared to bulk materials, if they possess strong new excitations, in particular of plasmon type. The confinement of excitations in the NPs leads to a (weaker and more gradual) additional cross section enhancement. Using *fs* laser pulses the confinement can also be temporally constrained which leads to additional nonlinear enhancements not possible on bulk crystals. The latter results also show that the time scales of the electronic

processes (including excitation and decay of plasmons) are very short, probably in the range below 10 fs, even though admittedly our results can only impose an upper limit of ∼100 fs. The dynamics of evolving molecular states, however, and thus the mechanism, appear essentially unchanged, at least for the case of our test system. This makes sense since these processes occur on much longer time scales. It cannot be excluded that there are systems in which the time scales can mix and, e.g., the plasmon excitation has a direct photochemical influence; in fact we have seen one such case for physisorbed xenon,[72] but this is probably a rare, unusual case. It should also be noted that in systems with competing photo-induced reaction channels the cross section enhancement can be different for different channels, even with constant mechanisms. We have in fact seen this for our $(NO)_2$ test system which as mentioned possesses other weaker channels.[73]

What can be carried over to practical photochemical processes? Obviously, the main advantage of the use of NPs will lie in the improved light harvesting which plasmon excitations make possible. Since plasmon resonances are rather narrow, even if the variations with particle size are utilized by using broadly varying ensembles, the usable part that can be caught of a broadband source like sun light will be limited. If one aims at photochemical reactions which require a certain minimum energy it is important to use NPs with plasmons in the required energy range. Alloy and core-shell NPs could be useful in this respect. Also, supports which do not lead to screening of the lower energy (1,1) parallel mode would be helpful - note that the use of ultrathin oxide supports in the reported experiments were dictated by convenience of experimentation and interpretation, not by necessity. On the other hand the use of supports which interact with the deposited NPs would be very interesting. For instance, for Ag NPs on strongly reduced $TiO_2$ supports plasmon excitation has been shown to lead to electron-hole pairs in the $TiO_2$ which decay radiatively.[74] The effects of confinement may depend more strongly on the particular system since they can be influenced by the photochemical mechanism which will not always consist in a TNI process. The subject of photochemistry at nanoparticles is a relatively young field and certainly will develop considerably in the near future.[75] There might well be NP systems which offer even new mechanisms of photochemistry, not just enhancements of those also occurring on compact materials.

## VII. CONCLUSIONS

This overview has shown a field which is quite mature in the existing knowledge and understanding, due to its considerable age which parallels that of modern surface science and to many sophisticated experimental and theoretical methods and concepts. The latest results show that embracing new classes of systems poses new challenges for the understanding as well as promises for its application. The future is bright for photochemistry at surfaces.

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