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REVIEW ARTICLE

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The authors give a survey of their work on photochemical processes at silver nanoparticles carried out in Berlin in the past decade. Using well established procedures for the preparation of silver nanoparticles (Ag NPs) supported on ultrathin alumina layers on NiAl single crystals, they have investigated the photoreactions of adsorbed $(NO)_2$ and of Xe induced by laser pulses. The authors examined the influences of photon energy (2.3, 3.5, and 4.7 eV) and polarization, mean particle size (2–10 nm), and pulse length (5 ns and 100 fs) on yields and cross sections, and on photoreaction mechanisms. Comparison with Ag(111) was made throughout. For the NO dimer layer, the authors find general agreement with known results on bulk Ag(111) in terms of possible reactions (NO desorption and NO monomer formation as well as conversion into adsorbed N_2O and O) and predominant mechanism (via transient negative ion formation, TNI); NO desorption is the strongest channel. However, on the NPs, the cross sections show selective enhancement in particular under conditions of excitation of the Mie plasmon due to the field enhancement caused by it, but—more weakly—also under off-resonant conditions which the authors interpret by excitation confinement in the NPs. For ns laser pulses, the desorption yield responds linearly to photon flux so that the cross sections are independent of laser fluence. Using fs laser pulses, nonlinear yield response is found under plasmon excitation which is interpreted as due to re-excitation of hot electrons in the NPs during a single laser pulse. The dynamics of the individual process, however, stay the same under almost all conditions, as indicated by constant energy distributions over translational, rotational, and vibrational energies of the desorbing NO molecules, even in the nonlinear range. Only for the highest photon energy (i.e., off-resonance) and the smallest particles, a new channel is observed with higher translational energy which is believed to proceed via transient *positive* ions. The branching into the various reaction channels is found to be different on Ag NPs from that on Ag(111) which is ascribed to differing enhancements for the various channels. While these results show that for a typical molecular reaction only the yields are modified on NPs, very different behavior is observed for desorption of adsorbed Xe. Here, low intensity excitation of the Mie plasmon leads to chaotic response which must be due to hot spot formation. As in this case no simple desorption mechanism (via transient negative or positive ions, or direct HOMO–LUMO excitation of the adsorbate) is expected, a direct action of the plasmon excitation is postulated. Some general conclusions are drawn from these case studies. © 2013 American Vacuum Society. [http://dx.doi.org/10.1116/1.4818425]

I. INTRODUCTION

Coupling of molecules to surfaces changes not only their ground state properties leading to strongly modified reactivity, which is the basis of heterogeneous catalysis with strongly modified activity and selectivity for chemical reactions, and many other surface effects. The same coupling also leads to changes of the electronically excited states of the adsorbates and consequent changes of photochemistry or more generally electronically induced reactions. This field of surface photochemistry has been investigated in great detail in the past 50 years on the surfaces of bulk crystals, and a vast amount of knowledge exists.[1–8] A large part of that work has centered on electronically induced desorption [often called desorption induced by electronic transitions, DIET (Ref. 6)] and has been concerned with electronic excitations by photons (including lasers and synchrotron light), electrons, or even ions. These processes are of basic interest but also of practical importance in surface structuring and similar processes. They can also be detrimental, e.g., in electron microscopy and electron spectroscopy; their investigation can improve the understanding of radiation damage. Extensive theoretical work has interpreted the detailed actions of the adsorbate–substrate

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coupling in the range of excitation and ionization, including curve crossing, localization and delocalization of excitations, and transfer of charge and energy between adsorbate and substrate. Many mechanisms have been proposed in response to particular findings, starting with the semiclassical MGR (Menzel–Gomer–Redhead) mechanism[9,10] and progressing to more refined and predictive mechanisms,[11,12] partly semiclassical, but some also fully quantum mechanical.[13–16]

Generally, an electronic excitation takes the system or the 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 potential energy surface (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. The system then evolves along the upper PES, and energy is transferred from the electronic to the nuclear modes of the molecule. This multidimensional evolution can lead to excitation of inner molecular modes (rotations and vibrations) and to photodissociation (more generally: electronically induced dissociation). The resulting fragments will usually possess hyperthermal translational energy and internal excitations; they can react with other partners encountered, so that electronically induced reactions occur. Crossing PESs add further complications leading to branching into variable reaction paths.

All this will also proceed on surfaces and concern adsorbates. Excitation and dissociation can now also happen to the adsorbate–substrate bond, in addition to internal bonds. Electronically induced desorption of the adsorbate or fragments of it, which can be neutral or ionic, can occur. Exchange of charge and energy between the molecules or fragments and the substrate surface can lead to important modifications, particularly on metal surfaces. These processes can be visualized as the corresponding wave packet jumping from one PES to another and can be described by crossing of (suitably shifted) PESs.[7–13] These complex evolutions modify the energy transfer along sloping PESs mentioned above. If such a process brings the system back to the ground state PES—albeit at a changed geometry—part of the evolution and energy redistribution can also occur on it. The substrate can serve as source and sink of energy and charge. In particular, short-lived charged excited states of molecules coupled to the surface, and their creation and destruction by charge transfer from/to the substrate, decisively influence the dynamics of electronically induced surface reactions (particularly on metal surfaces) compared to similar processes in isolated molecules.

An important distinction of electronically induced surface processes is whether the initial excitation (here the absorption of an incoming photon) happens in the adsorbate or in the substrate. If the adsorbate is present in a (sub)-monolayer, the absorption is generally stronger in the substrate; however, the photon may penetrate deeply and the excitation may be unlikely to return to the surface and become localized on the adsorbate, which is necessary to lead to a bond breaking event and further reactions. The former case of adsorbate-mediated surface photochemistry is possible at all energies; it is likely to dominate if the photon fits to a resonant excitation of the adsorbate. The dynamics is governed by the lifetime of the excitation on the adsorbate which is limited by its transfer to the substrate. At low photon energies and in the nonresonant case, the photon penetrates into the substrate producing many excitations in it; some of them can transfer to the adsorbate and lead to an excitation. This is the case of substrate-mediated surface photochemistry. In the most likely case of hot electron production in the substrate by visible or UV light, one of these hot electrons can be transferred to an adsorbate creating a (transient) negative ion on the surface.[11,17–19] This induces an attraction of the adsorbate to the surface, in addition to the excitation-induced modification of the adsorbate (Fig. 1). On a metal surface, the adsorbate will generally be accelerated toward the surface by image charge interaction, a modification of the surface bond by the excitation notwithstanding. This acceleration is active only while the transient negative ion formation (TNI) persists, which is expected to be very short. Note that the charge transfer back into the metal is equivalent to the reverse of quenching the excited adsorbate in the adsorbate-mediated case: charge transfer to and from the adsorbate are connected by microscopic reversibility.

Analysis of DIET processes has shown that the timescale of these processes is in the low fs to sub-fs range. This in fact makes the reaction efficiency of low energy excitations (leading to hot electrons below the vacuum level) on metal surfaces

(a)

(b)
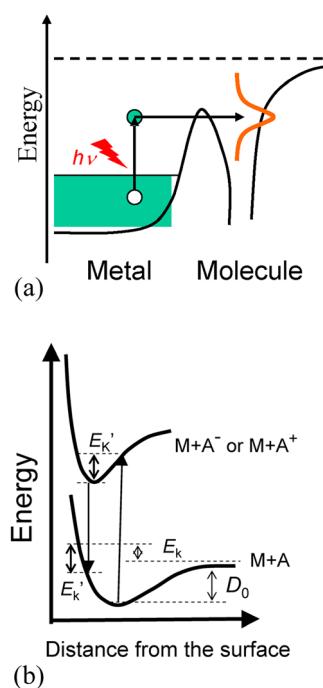
Fig. 1. (Color online) (a) Sketch of the TNI process. Visible or near-UV photons are absorbed in the substrate, a metal, and create hot electrons. These can collide with the surface and, if their energy fits, tunnel into an unoccupied level of an adsorbate, where they will reside only briefly and then 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 toward 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. Reprinted with permission from D. Menzel, J. Chem. Phys. **137**, 091702 (2012). Copyright 2012 American Institute of Physics.

very low. On the other hand, bombardment of an adsorbate-covered surface with photons or electrons of higher energy (say, above 50 eV) will always create a large flux of secondary electrons of broad energy distribution which can interact with adsorbates and induce reactions and damage when they exit the surface. This nonspecific action of secondary electrons is often called x-ray induced electron stimulated desorption (XESD). It is likely to be responsible for processes leading to radiation damage at surfaces and in thin films, in the latter case often by the TNI mechanism.[20,21]

This survey is structured as follows. Section II gives a short general outline of the specific effects expected by the use of nanoparticles compared to compact crystals. In Sec. III, we describe our results obtained for the photoinduced reactions of NO dimers adsorbed on Ag NPs and compare them to their parameters on Ag(111). We describe first the action of nanosecond laser pulses in terms of desorption efficiency for NO molecules, the distribution of energy over the degrees of freedom of the latter [which can be obtained by resonance-enhanced multiphoton ionization, REMPI (Refs. 22 and 23)] and their bearing for the desorption mechanism, and the NP effect for the other (minor) photoinduced channels in this system. Then, we summarize the corresponding results for femtosecond laser pulses in terms of efficiency and mechanism and describe a nonlinear mechanism possible only on NPs to explain the observed occurrence of nonlinear effects. Section IV describes our observations for photoinduced desorption of Xe atoms from adsorbed xenon on Ag NPs which has very surprising characteristics and discuss possible explanations. We emphasize that in the case of strong excitation mechanisms such as the TNI mechanism, the NP influence concerns mainly an increase of photochemical efficiency while the basic mechanism remains the same—even in the case of nonlinear enhancement. For weak excitations as those operating in the Xe case, basically new phenomena such as direct involvement of plasmons in desorption and hotspot formation by plasmonic coupling among NPs can occur.

II. PHOTOCHEMISTRY AT NANOPARTICLE SURFACES

The introduction has outlined the basis of electronically induced reactions on surfaces of extended substrates. They have mainly been investigated on well-defined single crystal surfaces in the surface science sense, with the aim being the detailed description and understanding of the underlying mechanisms. A different, very interesting, and practically important type of substrates are nanoparticles in the size range of up to about 100 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.[24]

It is a valid and interesting question whether on such MNP systems, reactions of electronically excited molecules will show properties characteristically different from those of the surfaces of bulk crystals. An examination of what is known about the excitations of MNPs has suggested that indeed definite changes of photochemistry (this term will be used subsequently because we are only concerned with photon excitation in the visible to near-UV range) can be expected compared to compact materials.[25,26] While many changes can be listed[26] which could lead to changes of photochemistry, the two most important ones to be expected concern new characteristic excitations—in particular, the strong Mie or particle plasmons[27,28]—on one hand, and on the other hand, the fact that excitations cannot as easily disperse into the bulk as on compact materials—an effect which can be called "excitation confinement." In the past decade, our group at the Fritz-Haber-Institut in Berlin has investigated in detail some test reaction systems directly comparing reactivities and mechanisms on NPs and on bulk material. The most extensive research[29–33] has been carried out on the photochemistry of NO dimers on silver surfaces, a comparatively complex system. A very differently behaving system was Xe adsorbed on the same Ag NPs.[34] We will briefly describe our methods, the main findings, and our conclusions from them. The results for the NO dimer system are believed to be fairly general for a photochemical system. For Xe/Ag NPs, a system without chemical interactions in the ground state, we find very unusual and probably untypical characteristics which must be due to NP properties and expand our knowledge of the possible NP influences.

III. PHOTOINDUCED DESORPTION AND REACTIONS OF (NO)$_2$ ON OXIDE-SUPPORTED Ag NPs

A. Systems and methods

In the following, we sketch the reasons for selecting this system, the prior knowledge about it, and the used methods and types of measurements carried out. For more details of the experimental systems and other methodological questions, see Refs. 29–36.

Since one of the expected important NP effects was the influence of Mie plasmons, the substrate chosen was silver which possesses a strong Mie plasmon.[27,28] An additional advantage was that the deposition of silver nanoparticles (Ag NPs) on ultrathin (2 monolayers) alumina films (on NiAl alloy surfaces) has been studied, and their properties have been characterized in detail in Berlin,[37] so that this detailed knowledge could be utilized. The preparation of narrowly defined particle sizes in the range 2–10 nm is possible on this type of substrate because Ag does not wet the defect-free, flat oxide surface: Ag vapor deposition leads to nucleation of NPs at defects only, as observed by STM and photon-STM.[37] Under suitable deposition conditions, the deposition dose then determines the size of the NPs in the range 2 to about 10 nm (bigger NPs show some agglomeration), with a width of the size distribution of 20%–30%; they have a roughly circular base with an aspect ratio of about 0.5. The surface density of defects (and therefore of Ag NPs) can be reproducibly influenced by the preparation details of the oxide layer; it was typically $\sim 4 \times 10^{11}$ cm^{-2} in our preparations. Such Ag NP layers possess a strong, rather broad plasmon excitation at ~ 3.5 eV (polarized perpendicular to the surface; the expected lower energy parallel mode is
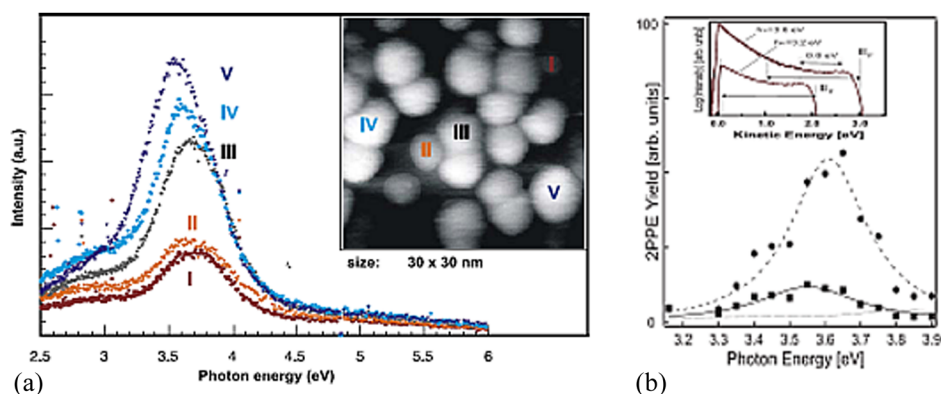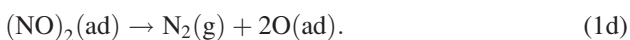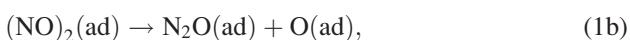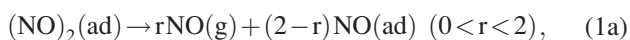
FIG. 2. (Color online) (a) Main figure: The photon emission spectra recorded by electron excitation of the NPs indicated as I to IV, showing the plasmon energy range and width, and the variation with size. Insert: Ag NPs on thin alumina films as seen in the photon STM, displaying NPs of varying sizes (I to IV). Reprinted with permission from N. Nilius, N. Ernst, and H.-J. Freund, Phys. Rev. Lett. **84**, 3994 (2000). Copyright 2000 American Physical Society. (b) 2PPE yield of 8 nm Ag NPs on ultrathin alumina vs photon energy (for two different integration ranges of the spectra; for details, see Ref. 38). Reprinted with permission from F. Evers, C. Rakete, K. Watanabe, D. Menzel, and H.-J. Freund, Surf. Sci. **593**, 43 (2005). Copyright 2005 Elsevier.

screened by the close-by metal substrate, further simplifying the analysis), as observed and characterized by photon STM (Ref. 37) and by two-photon photoemission (2PPE)[38] (Fig. 2). The thin alumina film decouples the Ag NPs quite efficiently electronically from the metal substrate; this should lead to excitation confinement. Nevertheless, no charge-up during electron spectroscopy or laser irradiation is observed, due to the thinness of the oxide spacer.[39]

For photochemistry, the frequently used NO was chosen as adsorbate because of the ease of its state-selective detection after desorption which has made it a frequent test adsorbate in photochemistry. On silver, however, NO adsorption is more complex than usually observed on (transition) metal surfaces. Its weak interaction with the (clean) noble metal necessitates 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[40] including their photochemistry[41] and influences on it from roughness.[42] These extensive earlier studies, which concluded that the photochemistry in this system proceeds via the TNI mechanism, provided a good basis for our experiments. Because of the dimer formation, the photochemical reaction channels are more complex than on transition metals, where only NO desorption and at high excitations some N-O dissociation are observed. Starting with the adsorbed dimers, it is found both thermally and photochemically that besides breaking of the ON-NO bond and the bond to the surface simultaneously—leading to NO desorption into the gas phase and leaving some monomeric NO on the surface which can also desorb—the dimers can also react to $N_2O + O$ which stay on the surface. As a minor channel, the desorption of fast N_2 has also been observed at high photon energy[30]

$$(NO)_2(ad) \rightarrow rNO(g) + (2-r)NO(ad) \quad (0 < r < 2), \quad (1a)$$

$$(NO)_2(ad) \rightarrow N_2O(ad) + O(ad), \quad (1b)$$

$$NO(ad) \rightarrow NO(g), \quad (1c)$$

$$(NO)_2(ad) \rightarrow N_2(g) + 2O(ad). \quad (1d)$$

N_2O formed by irradiation can be detected by subsequent thermal desorption. Adsorbed O strengthens its surface bond;[33,40] it also leads to a stronger bond of the NO monomer which then desorbs thermally at much higher temperature and has a much smaller photoreaction cross section than the dimer. We have characterized the layers on Ag(111) and on Ag NPs in the same system with temperature programmed desorption (TPD) and found good agreement for the former with the cited earlier work. Detailed analysis has shown that on the NPs, some of the dimer species seen on Ag(111) do not exist.[33] Investigating the influence of Ag NP size on the adsorption bond, we found[29,36] that with decreasing size, the desorption temperature decreased (see Fig. 3), with a roughly linear scaling of the TPD peak temperature, T_P, with the inverse NP size (in the lowest approximation, T_P is proportional to the desorption energy). This is
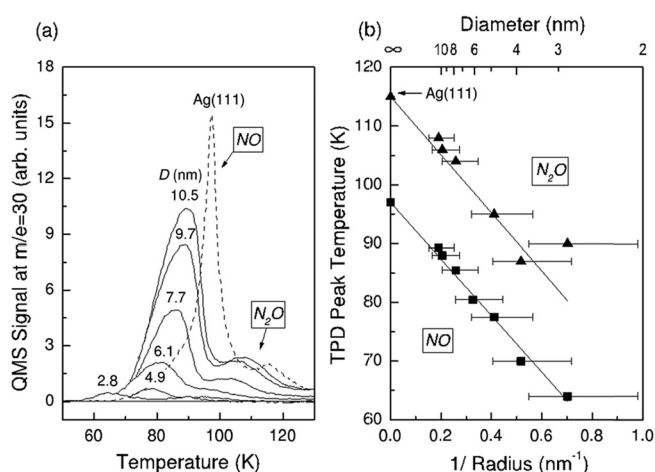
FIG. 3. (a) Size dependent TPD of NO from $(NO)_2$ on Ag NPs for different mean particle sizes as indicated. The dashed curve indicates the TPD peak from Ag(111). A similar set has been obtained for desorption of N_2O. (b) TPD peak temperatures as a function of inverse mean particle size [$1/R = 0$: Ag(111)] for thermal desorption of NO and N_2O. Approximate scaling with $1/R$ is seen. Reprinted with permission from D. Mulugeta, K. H. Kim, K. Watanabe, D. Menzel, and H.-J. Freund, Phys. Rev. Lett. **101**, 146103 (2008). Copyright 2008 American Physical Society.

understandable if the main bond stems from Van der Waals interaction, since this attraction integrates over all Ag atoms of an NP. Even for chemical contributions, this dependence is expected qualitatively. It has also been found for other systems, and its origin is discussed in detail.[43,44]

As to photochemistry we now concentrate on the strongest photoinduced channel, NO desorption. Measurements of yields and desorption cross sections as functions of photon energy (mostly for three photon energies: 2.3 eV, i.e., clearly below the plasmon excitation; 3.5 eV, i.e., on it; and 4.7 eV, clearly above it; in some cases also 4.0 eV were used) and polarization were carried out to characterize the NP influence on the photochemical efficiency and its size dependence. Here, the photodesorption cross sections (PCS) were derived from the semi-logarithmic decay of desorption signal with total fluence, as usual for a first order process of coverage decaying with irradiation

$$Y = A \exp(-\sigma N_{ph}), \qquad (2)$$

where Y is the desorption signal, N_{ph} is the irradiance (photons/cm^2), σ is the PCS (in cm^2), and A is a constant. We note that the pure NO photodesorption shows up in about the first half of dimer coverage removed (see Fig. 4 and Ref. 45).

In order to get information on the mechanism, the energy distributions over all molecular modes of the desorbing NO molecules were measured, the translational energy both by mass-selective time-of-flight measurements[29,33,35] and by delays of the REMPI signals,[31,36] and internal modes (rotation, vibration) by REMPI;[31,36] 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 instances.
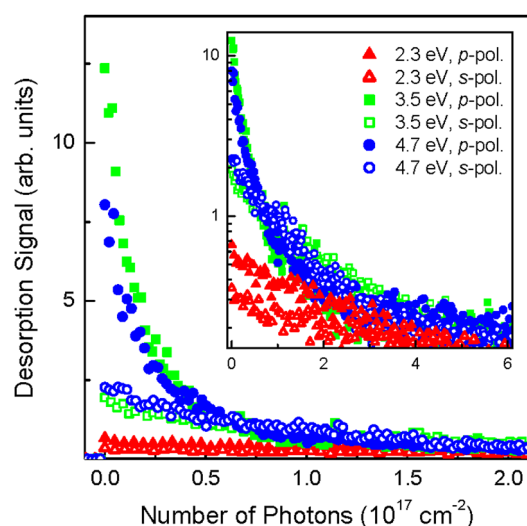

FIG. 4. (Color online) Irradiation decay of NO signals from NO dimer layers desorbed by ns laser pulses for the conditions given in the insert. Main figure: Linear scale; Insert: log plot of NO signal for extended irradiation which also identifies the symbols. For interpretation, see text and Ref. 45. Reprinted with permission from K. H. Kim, K. Watanabe, D. Menzel, and H.-J. Freund, Surf. Sci. **606**, 1142 (2012). Copyright 2012 Elsevier.

B. Results for NO dimers

1. NO desorption by nanosecond pulses

As already mentioned, the main photochemical channel for NO dimers on silver substrates is due to the breaking of the dimer bonds (both internal and to the surface) which leads to TNI-mediated desorption of ground state NO detectable by mass spectroscopy and REMPI. Some NO monomers remain on the surface which is connected with the presence of O adatoms from the minor channel $N_2O + O$ (NO monomers on a clean Ag surface are very weakly bound); they are also prone to photodesorption but with much lower cross section and different wavelength dependence than the NO dimers (see Sec. III B 3). In the following, we summarize the findings for NO photodesorption from NO dimers on Ag surfaces.

a. Desorption efficiency. The cross section, σ, for NO desorption, the main photochemical channel from $(NO)_2$ monolayers on Ag NPs,[45] is indeed strongly enhanced for excitations in the plasmon resonance (which as noted lies around 3.5 eV in p-pol., weakly dependent on particle size[37,38]). As shown in Fig. 4 and Table I, an increase of σ up to a factor 40 (depending on NP size; see below) relative to Ag(111) has been found.[29,33] This is understandable from the fact that the antenna effect of plasmons collects more of the incoming photons into the NPs. Many or most plasmons (depending on the NP size[26,28]) decay into electron–hole pairs by Landau damping[28] or, in the presence of adsorbates (as is necessarily the case in photochemistry), by chemical interface damping (CID).[26,28,46] In the latter process, a plasmon is quenched by dielectric interaction with an adsorbate via its LUMO,[46] creating also a TNI. CID shows up by a decrease of the strength of the plasmon-induced absorption. On the other hand, it has the same end result, so that both paths add up in a kind of compensating way for photochemistry via TNI; for the dynamics of desorption these two paths should be equivalent. Outside the plasmon resonance, only the hot electron route can exist.

TABLE I. PCS of NO from 8-nm Ag NPs and Ag(111) dosed with NO at 75 K measured at 2.3–4.7 eV (errors of PCS are between 3% and 25%, with larger values more accurate). Reprinted with permission from K. H. Kim, K. Watanabe, D. Menzel, and H.-J. Freund, Surf. Sci. **606**, 1142 (2012). Copyright 2012 Elsevier.

		PCS (10^{-18} cm^2)				
		(a) 8-nm Ag NPs		(b) Ag(111)		Enhancement factor, ratio
Photon energy (eV)	Polarization	PCS	p/s ratio	PCS	p/s ratio	(a) to (b)
2.3	p	2.1	1.5	0.86	2.2	2.4
	s	1.4		0.39		3.6
3.5	p	59	8.0	3.9	1.4	15
	s	7.3		2.8		2.6
4.0	Non-pol.	9.5	N/A	5.8	N/A	1.6
4.7	p	38	3.5	15	1.3	2.5
	s	11		12		0.9

Clearly an enhancement of σ exists at NPs also outside the plasmon resonance, albeit weaker (factors 2 to 3). This we assign to confinement of hot electrons in the Ag NP which here are produced directly by photon absorption in the NP (since no plasmon is involved here, CID cannot play a role). This confinement leads to an increased interaction of the hot electrons with the surface during their lifetime and enhanced adsorbate excitation. In a simple particle picture of the electron, this corresponds to increased collision numbers between hot electron and adsorbate due to the fact that the mean free path of the hot electron is considerably larger than the NP diameter.

The cross section enhancement depends on NP size [Fig. 5 (Ref. 29)]. Generally—i.e., off the plasmon resonance—it increases with decreasing NP size (diameter D or radius R), which is understandable by the mentioned confinement of the primary hot electrons in the NP ($\sigma \sim 1/D \sim S/V$, the surface/volume ratio). We emphasize that the desorption yield, Y, of course decreases with decreasing particle size, due to the decreasing total adsorbate coverage, but the desorption cross section, σ, which contains the relative coverage change [see Eq. (2)] can vary in any direction. For plasmon excitation, a strong maximum of σ at a certain NP size (here at $D \sim 5\,nm$) is superimposed. We have explained this by two main counteracting influences: on 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,[28] which is dominant for large particles; on the other hand, the total number of photons collected decreases with decreasing number of atoms in the particle.[28,29] There could also be a contribution of CID whose size scaling is unclear. Theoretical work[46] leads to 1/R scaling, while one experimental report[47] did not find an influence but investigated much bigger NPs than we use. Assuming 1/R scaling, the two p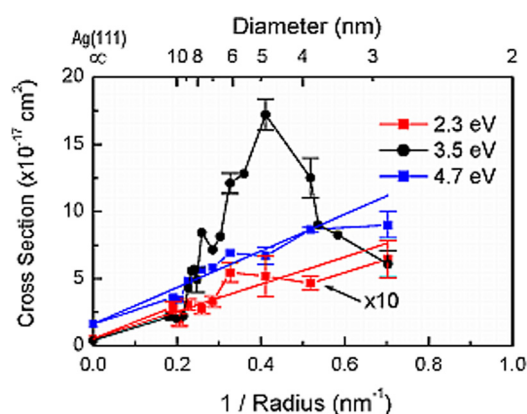aths to TNI cannot be separated by the scaling; we therefore include possible CID contributions under the hot electron mechanism in our discussion. Possible direct actions of plasmons will be discussed in Sec. V, where we will conclude that they should be important only for cases in which "normal" mechanisms are low. Considering other possible size-dependent effects,[26,29] there could be changes of the surface density of states with size; the hot electron lifetime varies in an energy-dependent way with size;[48] we cannot exclude that the adsorption sites and states change when going to small NPs, with steps and edges becoming important. All these influences are made improbable by the finding that the dynamics of the desorption appear to be constant—this is deduced from final state energy distributions, as will be described in Sec. III B 1 b—while changes would be expected if these effects were important.

b. Desorption dynamics and mechanism. As mentioned, the previous work on flat and rough Ag surfaces[41,42] had concluded that the photochemical mechanism involves TNI states. Our results for the energy distributions over the degrees of freedom of desorbed NO agree with this conclusion. We find translationally, rotationally, and vibrationally hot NO molecules (see Fig. 6). Translations and rotations are

FIG. 5. (Color online) Variation of desorption cross sections, σ, of NO from (NO)$_2$ monolayers on Ag NPs as a function of inverse mean particle size (for particle size see top abscissa), for the 3 photon energies given. For 2.3 and 4.7 eV (below and above the plasmon resonance), the cross section roughly scales with 1/R, i.e., with the surface/volume ratio. At ∼ 3.5 eV (p-pol.), the plasmon is excited, leading to much stronger enhancement and a clear maximum for particles between 4 and 6 nm. Reprinted with permission from D. Mulugeta, K. H. Kim, K. Watanabe, D. Menzel, and H.-J. Freund, Phys. Rev. Lett. **101**, 146103 (2008). Copyright 2008 American Physical Society.

FIG. 6. (Color online) Translational (top), rotational (center), and vibrational (bottom) energy distributions of desorbing NO vs inverse mean particle size [1/R = 0: Ag(111); size: top abscissa] for three photon energies. The inset in the top panel shows the appearance of a new fast component at 4.7 eV excitation for small particles which also possesses higher rotation and vibration. Top panel: Reprinted with permission from D. Mulugeta, K. H. Kim, K. Watanabe, D. Menzel, and H.-J. Freund, Phys. Rev. Lett. **101**, 146103 (2008). Copyright 2008 American Physical Society. Center, Bottom panels: Data from D. Mulugeta, K. Watanabe, D. Menzel, and H.-J. Freund, J. Chem. Phys. **134**, 164702 (2011). Copyright 2011 American Institute of Physics.

positively correlated (Fig. 7), while vibrations are decoupled. This is expected for the TNI mechanism: the transient negative ion formed when a hot electron created in the bulk tunnels into the LUMO of an adsorbed NO dimer is accelerated toward the surface on the excited state PES (Fig. 1). When the hot electron in its LUMO is transferred back to the substrate closer to the substrate, reflection occurs on the repulsive part of the ground state curve [Fig. 1(b)], leading to center-of-mass acceleration as well as a torque. The vibrational excitation, on the other hand, stems from the stretching of all bonds during the TNI lifetime (the LUMO acts repulsively on the N-O as well as the N-N bonds of the dimer), so that the molecule is left in a stretched state when the TNI decays and the desorbed NO fragment is vibrationally excited. These two energy transfer processes are independent of each other, explaining the coupling translation–rotation and the decoupled vibrations. Also, the wavelength dependences found agree with the TNI view. The LUMO of the adsorbed NO dimer has been calculated at $\sim 2\,eV$.[49] Indeed, only partial removal of the dimer has been found after prolonged irradiation with 2.3 eV light, while 3.5 and 4.7 eV light eliminates all dimers; the latter also deplete (partially or fully, respectively) the formed NO monomers suggesting that their LUMO lies around 3.5 eV.[33]

The most relevant result of the energy distributions for our main question, that concerning a possible NP influence on the mechanism of NO desorption, is that the latter is

(almost always; see below) the same on Ag NPs as on Ag(111). This is corroborated by the particle size independences of the final state energies (see Fig. 6). In particular for plasmon excitation, there is no change, even in the NP size range with the highest cross section enhancement. This means that the dynamics of the individual dissociation/desorption process 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 various evolving molecular entities, is the same on compact Ag(111) and on Ag NPs of varying sizes and is not influenced by the plasmon enhancement. This makes the other size-dependent influences mentioned at the end of the last section unlikely and shows that the enhancements only increase the probability of excitation but leave the dynamics and mechanism of desorption constant.

The only exception to this constancy of mechanism is found for excitation with the highest photon energy used (4.7 eV, i.e., off the plasmon resonance) and the smallest NPs (D < 4 nm), for which case the mean translational energy of NO was found to be considerably enhanced (see Fig. 6, top panel, in particular, the inset). In fact, closer inspection shows that a new much faster component was found in addition to the normal one;[29,31,36] singling out this component for REMPI also shows increased rotation and vibration (Fig. 6, two lower panels). The new path causing this component has been assigned to 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 (Fig. 8). This transient positive ion (TPI) path becomes observable only for very small NPs because its contribution is proportional to the surface area, while the TNI contribution goes down with the volume.[28,29,31] The detection of this new path from the energy distribution measurements corroborates their sensitivity to mechanistic changes, underlining in reverse the constancy of mechanism between compact surface and NPs and with particle size, for the plasmon-resonant case.

2. NO desorption by femtosecond excitation

The results described so far were obtained with nanosecond lasers (pulse length $\sim 5\,ns$) at fluences which lead to linear behavior of the photochemical yield with fluence, i.e., the determined cross sections are independent of fluence (this was safely the case for fluences up to at least 2 mJ/cm^2 per pulse). 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. For plasmon excitation, we found very different behavior when using femtosecond ($\sim 100\,fs$) laser pulses of the same (or even smaller) fluences. Now, the photons of a pulse arrive in a much shorter time, and the spatiotemporal photon density[35] is increased by at least a factor 10^4. The photon energy of the fs-laser used was 3.1 eV (p-pol.) which is at the rising edge of the plasmon resonance, at about 20% of the maximum[37,38] (Fig. 2); a correction has to be applied for this. Direct comparison was made with 5 ns pulses of
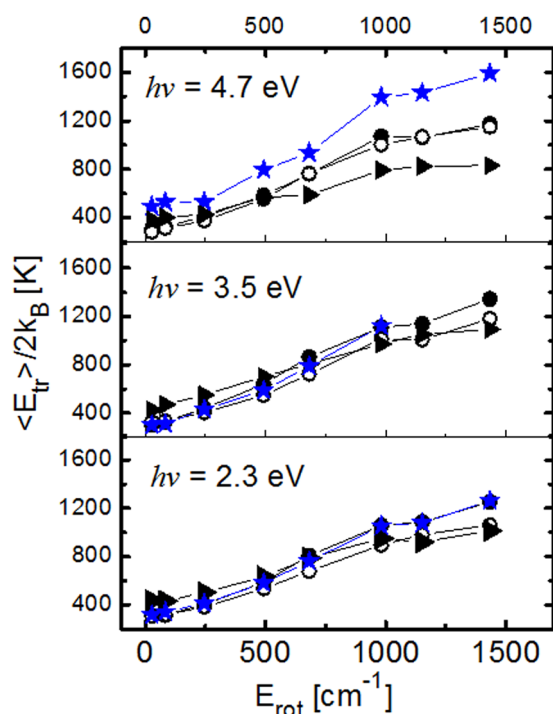

FIG. 7. (Color online) Correlation between mean translational and mean rotational energy for the photon energies given and for various sizes [from 4 nm Ag NPs (filled stars), 8 nm Ag NPs (filled circles), 11 nm Ag NPs (empty circles), and Ag (111) (filled triangles)]. The good, approximately linear correlation independent of conditions—except for 4 nm at 4.7 eV—is obvious. Reprinted with permission from D. Mulugeta, K. Watanabe, D. Menzel, and H.-J. Freund, J. Chem. Phys. **134**, 164702 (2011). Copyright 2011 American Institute of Physics.
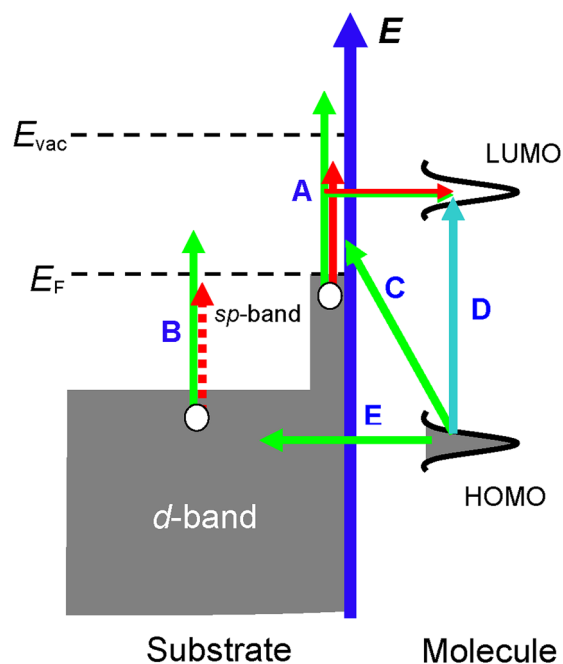
FIG. 8. (Color online) Sketch comparing the TNI at low excitation energy (arrow A) and the TPI mechanism becoming possible at higher energy (arrows B + E), either by internal creation of a d-hole which can ionize the HOMO of the adsorbate or by charge transfer excitation from the HOMO to the empty substrate DOS (arrow C). The arrow D indicates the direct HOMO–LUMO excitation in the adsorbate. Reprinted with permission from D. Mulugeta, K. Watanabe, D. Menzel, and H.-J. Freund, J. Chem. Phys. **134**, 164702 (2011). Copyright 2011 American Institute of Physics.

3.5 eV (p-pol.). 8 nm Ag NPs were used. Comparison was also made *in situ* with $(NO)_2$ on Ag(111) for identical conditions.

For plasmon excitation of the Ag NPs, the desorption cross section of NO is now considerably enhanced and increases with fluence; i.e., the yield has nonlinear fluence dependence [Fig. 9(a)]. The exact yield and PCS nonlinearities could not be determined because even by a single laser shot, the center of the laser profile on the surface is already depleted of NO, and further shots mainly spread the depletion within the profile; however, the exponent is certainly at least 2 for the PCS. For 3.5 eV, p-pol. light, this effect is visible already at low fluences ($\sim$0.1 mJ/cm^2). For fs pulses of the same energy but s-polarization, a small cross section increase was seen at much higher ($\times$10) fluence, while for ns pulses of 3.5 eV (p-pol., 2 mJ/cm^2) on 8 nm Ag NPs, and for both fs and ns pulses on Ag(111), the cross sections stayed independent of fluence [see Fig. 9(a)]. On the other hand, the constancy of translational energy distribution for ns and fs excitations [Fig. 9(b)] shows that the dynamics of desorption is again unchanged. 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 (Fig. 10).

So the nonlinearity is found only for plasmon excitation at the Ag NPs and is caused by a very short-lived interaction of hot electrons. The latter is not surprising since the
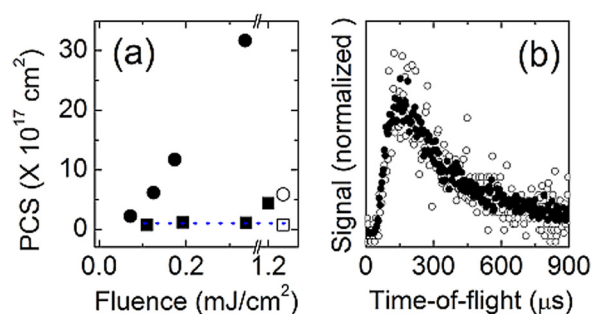

FIG. 9. (Color online) (a) Cross sections (PCS) for NO photodesorption from NO dimer layers by ns and fs pulses at low fluences. Filled circles: 8 nm Ag NPs, 3.1 eV, 100 fs laser pulses, p-pol. Filled squares: Same, but s-pol. Note break in abscissa to include high fluences. Open circle: 3.5 eV, 5 ns, p-pol. Open square, same, s-pol. The nonlinear behavior at low fluences for resonant excitation and the (near-)constancy of the PCS for the other conditions are obvious. (b) Time-of-flight results for the NO signal caused by ns (filled circles) and fs (empty circles) laser pulses. Despite the scatter for the latter, the equality of the two curves is obvious. Reprinted with permission from K. H. Kim, K. Watanabe, D. Mulugeta, D. Menzel, and H.-J. Freund, Phys. Rev. Lett. **107**, 047401 (2011). Copyright 2011 American Physical Society.

plasmon lifetime as well as that of the primary hot electrons produced by their decay is known to be shorter than 10 fs.[50,51] We have explained our observations by a re-pumping of hot electrons within the same pulse (Fig. 11) which becomes possible by their confinement in the NP.[32,35] This nonlinear enhancement is different from those discussed previously for photodesorption from compact substrates, the desorption by multiple electronic transitions (DIMET), and the friction mechanisms;[11,52–54] it is only possible on NPs. However, despite this dramatic change of reactivity, the translational energy of desorbing NO is again unchanged. This suggests that again the dynamics of desorption, as indicated by the NO final state energies, is unchanged. While the number of hot electrons in the individual NP which determine the frequency of attempts toward desorption increases drastically and nonlinearly, the individual process of molecular excitation and bond breaking is again the same. This finding also excludes possible paths via the DIMET or friction mechanisms, or nonlinear plasmon excitation, for which quite different energy distributions would be expected.

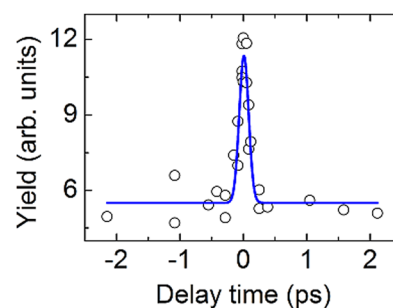FIG. 10. (Color online) Two-pulse correlation measurements of NO photodesorption from $(NO)_2$ layers on 8 nm Ag NPs for irradiation with 100 fs, 3.1 eV, 0.2 mJ/cm^2 pulses. The excitation lifetime is at most equal to the laser pulse length. Reprinted with permission from K. H. Kim, K. Watanabe, D. Mulugeta, D. Menzel, and H.-J. Freund, Phys. Rev. Lett. **107**, 047401 (2011). Copyright 2011 American Physical Society.
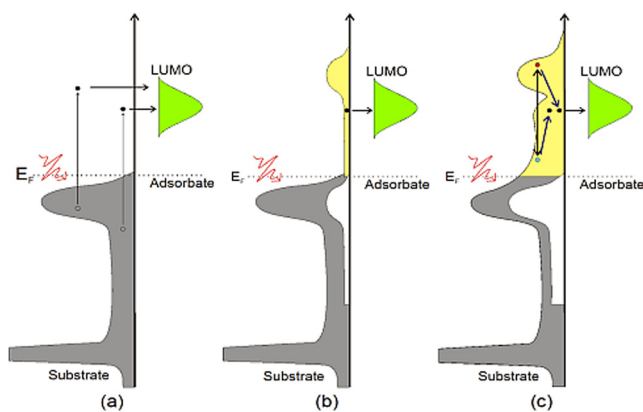
FIG. 11. (Color online) Sketch of suggested mechanisms for ns and fs excitation. (a) Single desorption attempt for adsorbate on NP (ns excitation). The most energetic hot electrons can can scatter into the LUMO, but after a single electron-electron scattering event, the hot electron cannot reach the LUMO any more. (b) Strong excitation by fs pulse increases the hot electron density with sufficient energy, but again a single scattering would quench this process, unless (c) the cooling hot electrons can be re-excited within the same laser pulse. Reprinted with permission from K. H. Kim, K. Watanabe, D. Mulugeta, D. Menzel, and H.-J. Freund, Phys. Rev. Lett. **107**, 047401 (2011). Copyright 2011 American Physical Society.

3. Other photochemical reaction channels of (NO)₂ on Ag NPs

As emphasized above, the coupled dissociation of $(NO)_2$ and desorption of NO is—while being the strongest channel—not the only photoreaction in this system. The formation of N_2O and adsorbed O from $(NO)_2$ is photochemically a dead end up to 3.5 eV, since N_2O stabilized by O(ad) is photoreactive only with 4.7 eV photons. Interestingly, pure N_2O on Ag(111) has been shown to be quite photoreactive, with complicated characteristics.[55] This shows the importance of the interaction between N_2O and O(ad).

The interaction with O(ad) is also important for the so-called NO monomers which are also photochemically formed by NO dimer dissociation. As pointed out before, this interaction is necessary to keep single NO molecules on the Ag surfaces. As described in Sec. III B 1, the TPD spectra have shown that these species are quite different on NPs than on Ag(111).[33] Also, it has already been shown (see Fig. 4) that this species is photodesorbed as neutral NO as well, albeit with a distinctly smaller cross section than NO desorption from the dimers.[45] This leads to a mixing of these channels in the detected NO at high total fluences, i.e., for small remaining dimer concentrations and large monomer accumulation. The initial approximately half of the coverage evolution under irradiation is almost exclusively due to dimers, while in the later stages, the two channels mix, and at low remaining coverages, desorption from monomers dominates. The photodesorption from monomers can also be separated from the dimers by heating the dimer layer to ~110 K or saturating the NP surface with NO at 130 K, since both treatments remove the dimers.

Looking at the TOF spectra of photodesorbed NO during the coverage evolution or for these pure monomer preparations shows that the NO from monomers is faster than that from dimers. Since, as described, the monomer desorption can be investigated without interference from the heated
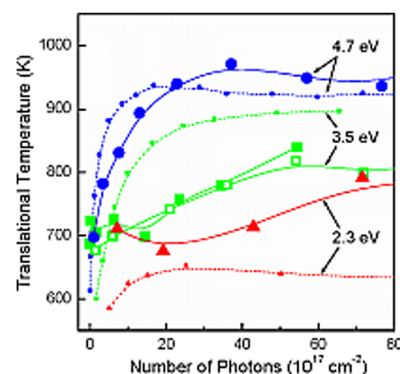

FIG. 12. (Color online) Evolution of the mean translational energy of desorbing NO from NO dimer layers on Ag NPs during irradiation, leading to transformation of the adlayer from dimers to monomers. The photon energies are indicated. Large symbols: Ag NPs; small symbols: Ag(111). Reprinted with permission from K. H. Kim, K. Watanabe, D. Menzel, and H.-J. Freund, Surf. Sci. **606**, 1142 (2012). Copyright 2012 Elsevier.

layers and the translational energy $\langle E_{tr} \rangle$ of NO from them obtained, the evolution of $\langle E_{tr} \rangle$ with irradiation (Fig. 12) can be used to extract the relative amounts of dimers and monomers during the evolution. For details of the analysis of the obtained data on the relative changes of the channels from Ag(111) to Ag NPs, we refer to Ref. 33. The main conclusion important in our connection is that while the relative importance of the channels is changed by using NPs, this is due to selective influences on the cross sections. No evidence for mechanistic changes has been found.

IV. PHOTODESORPTION OF XENON MONOLAYERS FROM AG NPS

The investigations described above about the modifications of surface photochemistry induced by the use of metallic nanoparticles, using the case of NO dimers on Ag NPs as a rather general example, have shown that the main influence of NPs is the cross section enhancement by plasmon excitation and excitation confinement, while the individual desorption dynamics and thus the mechanism are largely unchanged. This even pertains to the nonlinear range where the confined excitations can interact in a single laser shot. We believe that similar results can be expected for most, if not all photochemical processes mediated by transient charged molecular states. Here even the excitation of plasmons, a drastic modification of the excitation spectrum, does not appear to open new channels of coupling of the electronic and nuclear coordinates which forms the basis of photochemistry. The only report known to us from the literature suggestive of a direct plasmon influence on surface photochemistry is that of Träger *et al.*[56] who saw a plasmon-induced photodesorption effect of Na from Na NPs and interpreted it as a direct plasmon effect. Searching for such a direct influence we decided to investigate a system in which normal photochemical processes such as the TNI mechanism or a direct molecular excitation would not be possible which might lead to detectability of such a—possibly weak—effect. We selected the photodesorption of xenon atoms

from Ag NPs since for this adsorbate, the energy available in a photon coupling to the plasmon excitation can neither excite a TNI (there is no stable LUMO on the physisorbed Xe atoms[57]) nor can it induce a HOMO–LUMO transition of the Xe, the gap being around 9 eV. Indeed, Xe atoms on Ag(111) are not photodesorbed by 3.5 eV light, if laser fluences are sufficiently low to exclude thermal effects. So any special plasmon influences on Xe desorption from NPs should indicate a direct involvement of the plasmon. We indeed found such an influence, but the characteristics of the interaction turned out to be very unusual,[34] as will be described in the following.

Ag NPs of diameter 8 nm were prepared on thin alumina on NiAl(110) as described above. Their (1,0) plasmon resonance is at 3.6 eV. A Xe monolayer was prepared on them by Xe exposure at 20 K and subsequent heating to 61 K. The monolayer was irradiated by 2.3 or 3.5 eV laser light (p- or s-polarized) or unpolarized 4.0 eV light with pulse length 5 ns at 20 K. Desorbing Xe was detected by a quadrupole mass spectrometer with time-of-flight arrangement for translational energy measurements.[35] For p-polarized 3.5 eV light, a signal was measurable from 0.9 mJ/cm^2 pulses, s-polarized 3.5 eV or nonresonant wavelengths needed at least five times higher fluences for any detectable Xe signal. For the former, the TOF spectra (obtained by integrating over 500 shots) can be fitted by a component of 313 K and a smaller one with 43 K; for the latter, much smaller signals had energies around 160 K (Fig. 13). No photoinduced desorption was seen from monolayers of physisorbed CO or O$_2$ (thermal desorption at 60, respectively, 80 K) at pulses of 1 mJ/cm^2 nor from Xe multilayers. This proves that the Xe desorption from Xe monolayers on resonance is nonthermal,

while the effects off-resonance at higher fluences are probably thermal.

However, while the weak signals off-resonance as well as that on resonance with high fluences (>2 mJ/cm^2) showed the expected decrease under continued irradiation, the resonant signal at lower fluences showed erratic behavior (Fig. 14). The signal did not decrease monotonically but consisted of a herd of spikes with strongly fluctuating intensities. Such a behavior has never been observed under any conditions for the extensive investigations of NO dimer desorption and evolution, nor for the other conditions of Xe desorption, or for other physisorbates. The Fourier transforms of the data show a broad, decaying spectrum for the normal conditions but a flat spectrum without a peak for the fluctuating one. The latter is suggestive of a chaotic system.[58] Both the hyperthermal atoms and the chaotic fluctuations were suppressed if multilayers of Xe were used. This indicates that both properties are confined to Xe atoms in direct contact with the metal and are connected with plasmon excitation. That they are quenched for higher fluences at resonance must be due to them being covered up by the thermal signals dominating there.

We have argued that the chaotic[58] behavior is due to plasmonic coupling of suitably arranged sets of Ag NPs,[59] with fluctuating fields leading to the observed erratic switching. This coupling can lead to strong local field enhancements as well as increased lifetimes of the coupled plasmons.[59] Since we exclude thermal effects as well as a normal
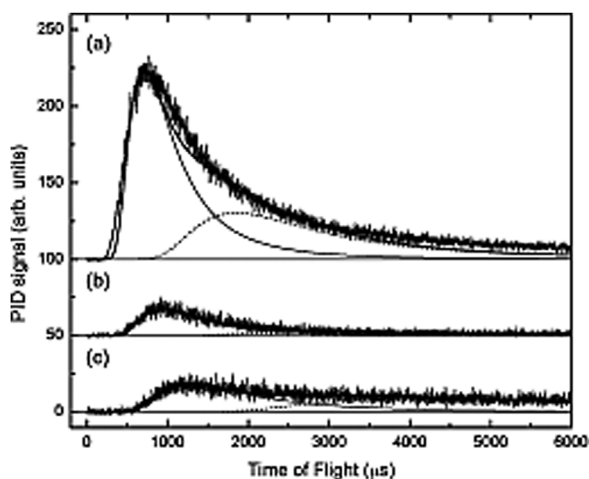

FIG. 13. Time-of-flight spectra of desorbing Xe atoms from (a) Xe/8 nm Ag NP by excitation in the (1,0) Mie plasmon resonance (3.5 eV p.-pol. light, 1.1 mJ/cm^2); (b) Xe/8 nm Ag NP by excitation off-resonance (4.0 eV unpol. light, 5.7 mJ/cm^2), ×2; (c) the bare alumina surface (3.5 eV p-pol. light, 4.9 mJ/cm^2), ×2. Fits by two shifted Maxwell-Boltzmann distributions are shown as thick solid, thin solid, and dashed curves for the sum, the fast, and the slow components. Reprinted with permission from K. Watanabe, K. H. Kim, D. Menzel and H.-J. Freund, Phys. Rev. Lett. **99**, 225501 (2007). Copyright 2007 American Physical Society.
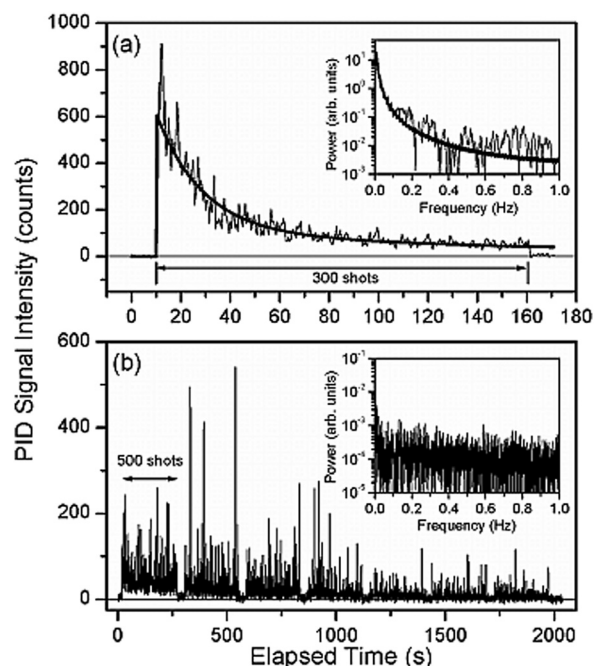

FIG. 14. Dependence of the Xe photodesorption signal from Xe/Ag NP on the total number of shots (2/s), given as time after irradiation start, for (a) excitation by 2.3 eV p-pol. light, 5.7 mJ/cm^2, 300 continuous shots; (b) excitation by 3.5 eV p-pol. light, 1.8 mJ/cm^2, with 1 min pauses after each 500 shots. The insets show the power spectra of the data obtained by Fourier transformation. Reprinted with permission from K. Watanabe, K. H. Kim, D. Menzel and H.-J. Freund, Phys. Rev. Lett. **99**, 225501 (2007). Copyright 2007 American Physical Society.

photochemical mechanism, the other property of this desorption, the hyperthermal Xe energies, suggests that a specific direct effect of the plasmon is responsible for the desorption seen. In Ref. 34, we have argued that this could be due to accumulated direct momentum transfer by the oscillating Pauli repulsion between the Xe electrons and the tails of the Ag s-electrons penetrating into the vacuum and moving with the plasmon frequency. For a simple model, we showed that about 300 collisions of the Xe with the moving "Pauli wall" (cycle time about 1 fs) are necessary to desorb a Xe atom. In view of the short plasmon lifetimes,[44,45] a lifetime increase of the plasmon by coupling[59] would then be necessary which would connect the two unexpected effects. We note, however, that other modes of interaction of the plasmon with the Xe might be possible, for instance, a dielectric coupling or a kind of frictional effect from the oscillating electrons in the plasmon. Unfortunately, no progress in understanding has been made in the 5 yr since these results were published. Theoretical efforts would be very welcome.

V. CONCLUSIONS AND SUMMARY

This survey has summarized results on two quite different adsorbate systems on Ag NPs. The NO dimer system is a fairly typical one in which low energy (visible to near UV) photochemistry is driven mainly by hot electrons photoexcited throughout the NPs and causing TNIs of the adsorbate. While TNIs can also be produced directly by CID, most if not all our results can be understood on the basis of hot electron production, and these possible two paths to TNI cannot be distinguished by our experiments. The constancy of dynamics found corroborates this. The results described above and their analysis have shown 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 which decay into electron–hole pairs. The confinement of excitations (hot electrons) in the NPs leads to an additional (weaker and more gradual) cross section enhancement for particle sizes small compared to the mean free path of the hot electrons. If the spatiotemporal density of excitations in the NPs is strongly increased by using fs laser pulses, the excitation 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 around or even below 10 fs, even though admittedly our experimental results can only impose an upper limit of ~100 fs. On the other hand, detailed examination of the distribution of energy over the molecular modes of desorbing NO have shown that the dynamics of evolving molecular states, and thus the individual mechanism, are essentially unchanged, even for the nonlinear range (only under very special, nonresonant conditions, evidence for a different mechanism has been seen which has been proposed to proceed via TPI). This makes sense since these dynamical processes occur on much longer time scales. We also note that in systems with competing photoinduced reaction channels, the cross section enhancement can be different for different channels, even when mechanisms are unchanged compared to the surfaces of bulk crystals. We have in fact seen this in our $(NO)_2$ test system for its other weaker photochemical channels.

These findings do not exclude the existence of systems in which the time scales can mix, so that, e.g., the plasmon excitation plays a direct role for photochemistry. The other case described above, photodesorption of physisorbed xenon, is such an example. It is an untypical case because none of the normal fast excitation channels (substrate-mediated via TNI or TPI; direct excitation of the adsorbate) are possible for it in the energy range concerned. We have suggested that indeed there is a direct action of the plasmon in photodesorption. This may proceed via concerted Pauli repulsion of the plasmon-induced moving surface charges (an oscillating Pauli wall) as suggested in our original publication or via dielectric or frictional coupling. An important point is that this is a very weak channel which becomes observable only because other channels are not operative. This fact is likely also the reason for the other unusual observation for this system, the chaotic behavior of the desorption signal which we interpreted by hot spot formation, i.e., by an enhancement beyond the normal plasmon enhancement and enhanced plasmon lifetime. This corroborates that we have found here a very untypical case.

What aspects of our findings are important for practical applications of NPs for 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 their variation with particle size is utilized by using ensembles with broadly varying sizes, the usable part that can be caught of a broadband source like sun light will be limited. Further, since photochemical reactions will require a certain minimum energy, it is important to use NPs with plasmons in the required energy range. Tuning of these energies could be done using alloy and core-shell NPs. Also, supports which do not lead to screening of the lower energy (1,1) parallel plasmon mode would be helpful; we note that the use of ultrathin oxide supports in our experiments were dictated by convenience of experimentation and interpretation not by necessity. The use of supports which interact with the deposited NPs would be very interesting also for other reasons: there may be supports for which the excitations of the NPs and of the support interact. For instance, it has been shown that plasmon excitation of Ag NPs on strongly reduced TiO_2 supports lead to electron–hole pairs in the TiO_2, which decay radiatively.[60]

The other NP enhancement effect via confinement of excitation may depend more strongly on the particular adsorbate system since it will be influenced by the interaction of the NP excitation with adsorbates which may not always consist in a TNI process. So, while we believe that our two described case studies map out the extremes expectable, there might well be NP systems which offer even new mechanisms of photochemistry, not just enhancements of those

also occurring on compact materials.[61] The young field of photochemistry at nanoparticles will certainly see considerable development in the near future.

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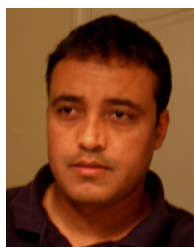
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