Size Effects in Thermal and Photochemistry of (NO)$_2$ on Ag Nanoparticles

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NO dimers adsorbed on alumina supported silver nanoparticles (Ag NPs, radii $R \sim$ 1–6 nm) show decreasing desorption temperatures and complex behavior of photoinduced desorption with decreasing NP size. In particular, for resonant excitation of the $(1, 0)$ Mie plasmon at 3.5 eV the photoinduced desorption cross section increases with $1/R$, showing a pronounced enhancement (40 times) at $R \sim$ 2.5 nm compared to Ag(111). At 4.7 eV the translational temperature of photodesorbed NO increases strongly with $1/R$. We discuss these trends and peculiarities in terms of the size-dependent properties of the Ag NPs.

Size effects in small clusters or nanoparticles (NPs) of metal atoms have been the focus of keen interest in various fields of physics and chemistry. For many properties interesting oscillatory behavior is found for the metal cluster (MC) range (up to about 100 atoms, or radius R about 0.5 nm), while for metal nanoparticles (MNPs) (above the cluster range) for many properties simple scaling laws with some power of reciprocal radius, $(1/R)^m$, have been found [1]. The size dependence of electronic structures of free MCs and MNPs have been extensively studied by photo-electron spectroscopy [2]. Strong changes are found to the optical response of MNPs in the range of the Mie plasmon [3]. Chemical properties of MCs and MNPs also show interesting size effects; e.g., the catalytic properties of Au clusters exhibit strong size dependence [4].

Here we focus on the NP size range. We address the question of how the photochemistry of molecules on MNPs changes with the particle size. A vast amount of accumulated knowledge exists for the photochemistry of small molecules on well-defined metal and semiconductor surfaces [5,6]. In the range of valence excitations, direct photoexcitation of adsorbates on metal surfaces is weak and rapidly quenched, and photochemistry is generally excited by hot electrons created by photoabsorption in the metal substrate which can be transferred to the adsorbate to become reactive: the transient negative ion (TNI) formed is attracted by its image charge and ends up in a repulsive state when the hot electron hops back into the metal; this leads to desorption [7]. The rapid quenching of these excitations makes cross sections small. For MNPs a number of influences can change this. The confinement of electronic excitations in them may already lead to enhanced photoreactions [8]. On alkali and coinage metal NPs, photochemical yields can be strongly increased in the range of plasmon excitations due to field enhancement as in surface enhanced Raman spectroscopy [9,10]: plasmon field enhancement of photoinduced desorption (PID) of NO from roughened [11] and particulate Ag surfaces

[12] have been reported. On the other hand, we recently reported *direct* influences of plasmon excitation for PID of Xe on Ag NPs leading to chaotic behavior explained in terms of hot spots by plasmonic coupling, and a new desorption mechanism [13]. The understanding and control of the complex physical and chemical properties of MNPs and their size dependences contain a potential for tailored photochemistry [14]. So far there is no systematic size-dependent study of photochemistry of molecules on small MNPs with well-characterized optical properties and electronic structure.

In this Letter we report on the size effects of photo-desorption of (NO)$_2$ adsorbed on well-characterized Ag NPs deposited on thin Al$_2$O$_3$ films on NiAl(110). The optical properties and electronic structure for Ag NPs (diameters 2–12 nm) are known from photon STM [15] and two-photon photoemission spectroscopy [16] showing their $(1, 0)$ Mie plasmon resonance at $\sim$3.5–3.6 eV. NO molecules adsorbed on silver surfaces at low temperatures (below 90 K) form adsorbed dimers which are photoreactive at photon energies as low as $\sim$2 eV, qualitatively similar to Ag(111) [17–19]. As we show below, their adsorption energy and photodesorption characteristics do change with decreasing size. The most interesting part of our findings is the occurrence of dependences which do not follow a simple scaling. Anomalously strong size dependences will be demonstrated for the PID cross section of NO in the Mie plasmon resonance, and for the PID dynamics at 4.7 eV. Our aim is to interpret these effects in terms of the size dependences of decay channels of the plasmon and of the *e-h* pairs in the Ag NPs.

The experiments have been performed in a UHV system described earlier [13]. Ag NPs were formed by depositing Ag atoms from an electron beam evaporator on an Al$_2$O$_3$/NiAl(110) substrate; roughly hemispherical Ag NPs with average radii (R) of 1–6 nm (standard deviations of at most 30% as known by previous STM observations [15]) resulted. (NO)$_2$ monolayers were formed by dosing

NO at 75 K to the saturation coverage of the monolayer of NO dimers and cooling to 40 K [20]. These layers were characterized by temperature programmed desorption (TPD) (heating rate 0.5 K/s) with a quadrupole mass spectrometer (QMS). Photoreactions were induced by irradiation with the second, third, or fourth harmonics of a nanosecond Nd:YAG laser (2.3, 3.5, and 4.7 eV, p-polarized, incident angle 45°, 1–2 mJ/cm^2). Photodesorbed NO molecules were detected along the surface normal by another QMS with a liquid nitrogen-cooled shroud, at a sample-ionizer distance of 19 cm. The signals at $m/e = 30$ were recorded simultaneously by two multichannel scalers with dwell times of 0.8 μs and 2 ms triggered by the laser pulses, to obtain time-of-flight (TOF) spectra and shot dependences of total PID yields of NO, respectively. Photodesorption cross sections were determined from the decay of PID signal with irradiation.

The thermal reactions of NO on Ag NPs possess clear size dependences as shown in TPD results of Fig. 1(a). The desorption peaks from the Ag NPs shift to higher temperatures with increasing size and approach those from Ag (111). The two mass 30 peaks [e.g., at 97 and 115 K in the case of Ag(111)] stem from desorption of NO and of N$_2$O (cracking in the QMS), respectively. The former stems from partially desorptive dissociation of NO dimers, concurring with the surface reaction to N$_2$O + O; desorption of the N$_2$O leads to the second peak [18]. Figure 1(b) plots the TPD peak temperatures T_p of masses NO and N$_2$O as functions of $1/R$. The data from Ag(111) are shown at $1/R = 0$. Interestingly, approximately linear relationships between T_p and $1/R$ are seen for both NO and N$_2$O, except for the smallest size for the latter.

The observed size dependence of the T_p suggests a corresponding change in adsorption energies E_{ad} (although a change of preexponential cannot be excluded). As space does not allow a detailed discussion and this aspect is not our main objective, we simply take the T_p values as semi-quantitative indication for the adsorption bond strength. Its decrease with decreasing NP size likely contains contributions from (i) changes of the van der Waals attraction, (ii) possible weakened chemisorptive contribution by the change of Ag surface states, and (iii) a shift to larger distances of the repulsive part of the surface interaction, due to increasing spillout of the Ag surface sp electrons for smaller NPs [21]. The details of these contributions need further investigation, but the similar scaling of the two peak temperatures is a notable result.

Photodesorption cross sections (PCS) of NO from NO dimers on the Ag NPs also show marked dependences on NP size. The data obtained are plotted as a function of $1/R$ in Fig. 2(a) for excitation energies of 2.3, 3.5, and 4.7 eV in p polarization, including those on Ag(111) [19] at $1/R = 0$. At 2.3 (4.7) eV, the PCS enhancement factor f
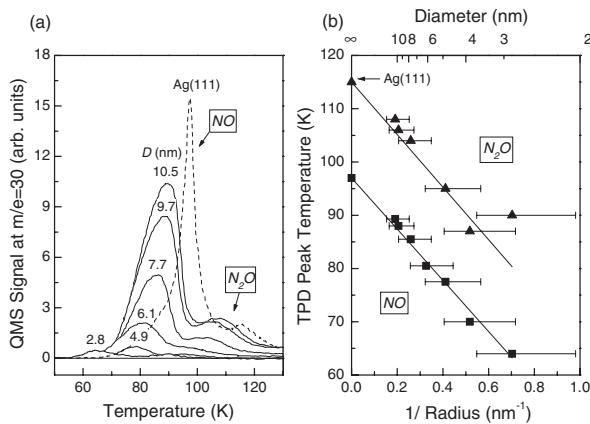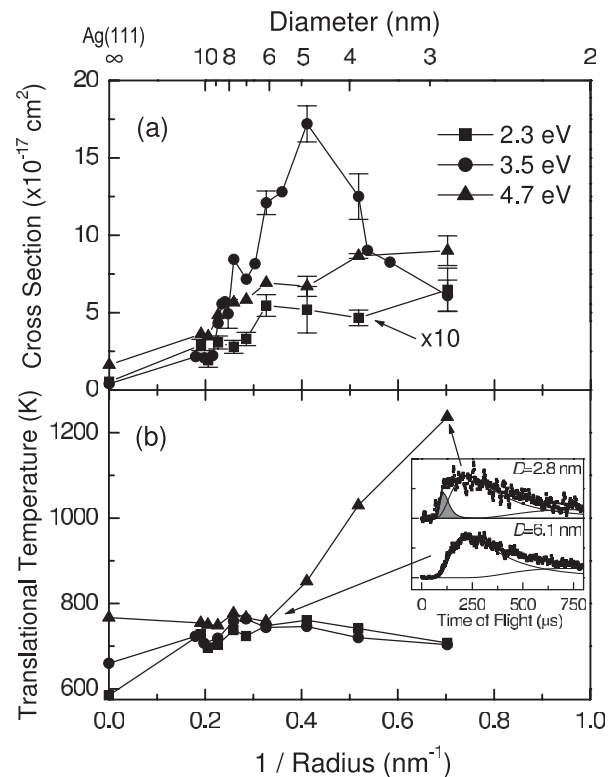

FIG. 1. (a) Temperature programmed desorption (TPD) results measured at $m/e = 30$ from Ag NPs of various diameters (D) dosed with NO at 75 K. The dashed curve shows a rescaled TPD result from Ag(111) for comparison. (b) Desorption peak temperatures of NO (squares) and N$_2$O (triangles) in (a) as a function of reciprocal radius, $1/R$ ($R = D/2$). The solid lines are linear fits for $1/R$ between 0 and $\sim$0.5 nm^{-1}. The error bars indicate standard deviations in the distributions of D.

FIG. 2. (a) Photodesorption cross sections of NO from Ag NPs as a function of $1/R$ (R is the mean radius of Ag NPs) at $h\nu =$ 2.3 (squares, multiplied by 10), 3.5 (circles), 4.7 eV (triangles). (b) Translational temperatures (T_t) of NO photodesorbed from NO dimers adsorbed on Ag NPs at 2.3 (squares), 3.5 (circles), 4.7 eV (triangles). Inset: Time-of-flight spectra for 4.7 eV excitation, fitted to a sum of shifted Maxwell-Boltzmann distributions ($T_t = 2700$, 750, and 70 K for peaks at 110 (in gray), 230, and 750 μs, respectively), measured for $D = 2.8$ and 6.1 nm.

with respect to Ag(111) increases gradually from 5 (2) at $1/R = \sim 0.2$ nm^{-1} to 12 (6) at $1/R = \sim 0.7$ nm^{-1}. For these nonresonant excitations the main difference from Ag(111) is that electronic excitations are confined in the Ag NPs by their small size and the insulating Al_2O_3 film. The increase of photoreaction efficiency with $1/R$ can be understood by the surface-to-volume ratio ($S/V \propto 1/R$). According to the TNI mechanism NO dimers are excited by hot electrons photogenerated within the Ag NPs, so the PCS is expected to scale with the collision number of hot electrons with the surface, analogous to the S/V effect for optical properties of MNPs in the classical model [22] given as v_F/R, where v_F is the Fermi velocity.

On the other hand, the PCS at 3.5 eV rises much more steeply with $1/R$, but then drops abruptly: f increases from 5 at $1/R = \sim 0.2$ nm^{-1} to 43 at $1/R = \sim 0.4$ nm^{-1}, and then drops to 15 at $1/R = \sim 0.7$ nm^{-1}. At 3.5 eV in p polarization, the (1, 0) Mie plasmon of the Ag NPs [15,16] is excited, enhancing the surface electric field at the Ag NPs. For $D > 20$ nm the plasmons decay mainly by photon emission, whereas Landau damping of plasmons into single electron-hole (e-h) pairs (with the hot electrons exciting the adsorbate) becomes more efficient for decreasing D and dominant at $1 \leq D \leq 4$ nm [23]. Thus, the steep rise of PCS up to $1/R = 0.4$ nm^{-1} is mostly attributable to the increasing share of Landau damping leading to electron-hole pairs which scales with v_F/R [24]. At $1/R > 0.4$ nm^{-1} ($D < 5$ nm), the Landau damping saturates. The total plasmon oscillator strength decreases with the total number of atoms in the NP, i.e., with V, according to Mie theory [25] as well as experiment [16] which explains the steep drop. Finally, f settles to the value of 15 at $1/R = 0.7$ nm^{-1}, which is comparable to those without plasmon excitation and attributable to confinement.

This interpretation mentions only the most important contributions. The situation is certainly more complex. First, Landau damping decreases the field enhancement, so that the increase of the share of e-h production in plasmon decay is partially compensated. Secondly, the presence of adsorbates decreases the field enhancement as well (chemical interface damping [26]), but this happens by scattering of hot electrons through molecular resonances, i.e., exactly by the process which leads to TNI formation and thus to desorption [14]. And thirdly, there are size influences on the spillout and screening at the NP surface [24,27] which are also superimposed. Only a very careful theoretical analysis might be able to disentangle all those contributions; even that might be difficult and would be model dependent. Therefore we can at present not go beyond stressing the strongest effects.

Size effects in desorption *dynamics* have been investigated by measuring TOF spectra accumulated from 1 to 100–200 laser shots. The translational temperature (T_t) of the nonthermal component was calculated by fitting of the TOF spectrum to a sum of shifted Maxwell-Boltzmann

distributions [7]. Results are plotted in Fig. 2(b). The T_t measured at 2.3 and 3.5 eV are 700–750 K, almost independent of size within the experimental error. The PID mechanism is thus constant throughout, even for excitation via the Mie plasmon. This stresses that in this system the plasmon is mainly active via the field enhancement. The found size dependences of the thermal reactions (Fig. 1), suggesting some change of the ground state, are seen to have no sufficient influence on these dynamics.

At 4.7 eV, on the other hand, a drastic change of T_t is seen for small particle sizes. T_t is almost constant at ~ 750 K until $1/R = 0.3$ nm^{-1}, but it then increases almost linearly to 1200 K at $1/R = 0.7$ nm^{-1}. In fact the change is even more drastic: In addition to the nonthermal ($T_t = 750$ K) and the thermalized components ($T_t = 70$ K) in the TOF spectrum (inset of Fig. 2) for larger R, a faster component with $T_t = 2700$ K grows for smaller R. This extraordinary size dependence of T_t occurring only at 4.7 eV for small R invokes the emergence of a new photodesorption channel with different dynamics leading to much faster desorbates than the normal hot electron-mediated TNI mechanism.

At 4.7 eV, excitations from the Ag d band (~ 4 eV below the Fermi level, E_F) to empty sp states above E_F are possible. Since the adsorption bond of $(NO)_2$ on Ag most likely involves some hybridization of Ag d electrons with dimer a_1 states [28], production of holes in these d states at the surface could lead to a transient *positive* ion (TPI). These holes, created throughout the NP, must become localized at the surface to be able to ionize the adsorbate hybrid. This will be more efficient for smaller R due to the $1/R$ effect. To be sure, a photon of 4.7 eV ($>\Phi$, work function of Ag NPs) can create a hole also in the sp band near E_F by photoelectron emission. However, this process cannot explain the peculiar increase of T_t with $1/R$ at 4.7 eV, as there are no adsorbate states around E_F; also,Φ will increase with $1/R$ rather than decrease. In addition, the production of sp holes near E_F is not a new channel, as it is possible even at lower photon energies. In the case of TPI, the translation energy can be higher than in the TNI case. Again, attraction by the image charge will accelerate the TPI towards the surface, but because the radius of a TPI is smaller than that of a TNI, it can approach the surface closer before neutralization. Thus, the repulsion activated then leads to much higher translational energies than for the hot electron TNI process, in agreement with our observation. To the best of our knowledge, the TPI mechanism has not been reported in photodesorption from bulk metal surfaces, which is probably due to the dominant contributions of the TNI produced by hot electrons from deep in the bulk.

In conclusion, in an investigation of thermal as well as photochemical properties of NO dimers adsorbed on Ag NPs of varied size on alumina, we have found size dependences with simple scaling as well as with peaked behavior or abrupt changes. The peak temperatures T_p of thermal

desorption of NO and N_2O from these layers decrease with decreasing size and show a simple linear scaling law with $\sim 1/R$ to good accuracy. This suggests a decrease of the adsorbate binding with decreasing size. For the PID cross sections of NO we find roughly an increase with $\sim 1/R$ for nonresonant excitation (photon energies 2.3 and 4.7 eV). However, for excitation in the plasmon resonance (3.5 eV, p-polarized) a strong peak at $R \sim 2.5$ nm is seen which can be considered as superimposed on the general $1/R$ behavior. Measurement of the translational energies of the photodesorbed NO corroborates that the accepted mechanism, TNI formation by hot electrons, persists throughout the NP size range for 2.3 and 3.5 eV, so that the main influence of plasmon excitation is an increase of hot electron excitation only, in contrast to Xe on Ag NPs [13]. At 4.7 eV and small R, however, an anomaly—a new component in the TOF spectra corresponding to ~ 4 times higher desorbate energies—indicates contributions of a new mechanism. We argue that this consists in formation of hot holes in the d band at the Ag NP surface which can lead to desorption via transient positive adsorbate ions.

We believe that this work, which is the first detailed investigation of its kind, shows the potential of size influences in photochemistry of MNPs. We hope it will trigger efforts for better understanding of the underlying complex phenomena.

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