Dynamics of O₂ photodesorption from metal clusters: A significant difference from bulk behaviour

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Abstract

Photodesorption of O₂ from size-selected Ag_nO₂⁻ cluster anions with $n = 2, 3, 4$ and 8 was studied using time-resolved photoelectron spectroscopy (TR-PES). The spectra indicate that relaxations of photo-excited Ag_nO₂⁻ clusters with $n =$ even numbers accompany ultra-fast *direct* O₂ photodesorption. For the odd-numbered cluster Ag₃O₂⁻, in contrast, a *long-lived* excited state is observed, since O₂ might be dissociatively chemisorbed, suppressing direct photodesorption of oxygen. Both, *direct* desorption and *long-lived* excited states, have not been observed from adsorbate covered metal surfaces, suggesting unique photochemical properties of such small clusters.

Photons can interact with matter in various ways, and one well known example for a photon-induced process is desorption of molecules, such as O₂ and CO, from metal surfaces [1]. In almost all cases this process occurs indirectly, i.e. the energy of the photon is first thermalized resulting in either hot conduction electrons and/or phonons, which can subsequently drive the desorption process [2,3]. The direct process via excitation of an electron into an antibonding orbital localized at the molecule is rather unlikely for metal surfaces, because relaxation of the excess energy of the photon is an extremely fast process [1]. The energy of an excited state is dissipated among the conduction electrons of the metal surface, quenching the state within less than 50 fs [4]. An electronic excitation is too short-lived to cause desorption, which is quenched even before the nuclear motions of the molecules start. The subsequently created hot electrons can lead to desorption; however, with increasing time after photoexcitation, the desorption process becomes less likely due to the increasing energy dissipation into the bulk. In summary, a very low

quantum yield can be found for photodesorption from a metal surface.

For clusters of simple metals (e.g., Na_n, Ag_n, $n =$ number of atoms) the situation is different: The density of states is low, resulting in lifetimes for excited states in the time-scale of nanoseconds [5–8]. In general, major relaxation channels are (i) electron–electron interactions (Auger-like processes), (ii) electron–phonon interactions and (iii) internal conversion. Processes (i) and (ii) become slower in clusters because of the low density of states. Similar to the case of molecules, only internal conversion can still be a fast process [9]. For clusters, therefore, two major relaxation channels are hindered and excited states could have longer lifetimes, increasing the probability of direct photodesorption. In this case, clusters can become interesting in photochemistry.

So far, direct photodesorption of molecules from metal clusters has not been observed. The few experimental observations [10,11] all proved to be dealing with thermal desorption rather than a direct process: The energy of the photon is thermalized within less than 100 fs, and in a subsequent step, the molecule desorbs from the hot cluster via unimolecular dissociation. In that case, the initial electronic excitation is quenched extremely fast. A possible

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relaxation process explaining these observations is internal conversion [9]. Its probability depends on the coupling between electronic and geometric structure, which are different for each cluster and molecule. It is expected that clusters with a rather rigid structure like gold- or metal-oxide clusters show no or much slower internal conversion compared to Ag_n^- or Al_n^- , since shape deformations, leading to internal conversion [9], are hampered. We have been aiming in finding an example of such a cluster with slow internal conversion, which should exhibit *long-lived* excited states and a high probability for direct photodesorption.

We studied Ag_nO_2^- clusters with $n = 2, 3, 4$, and 8 using time-resolved photoelectron spectroscopy (TR-PES). After photoexcitation by a 3.1 eV photon, Ag_2O_2^- decays on a time-scale of <100 fs by *direct* photodesorption into Ag_2^- and O_2 . The desorption proceeds via a transient excited state giving rise to a pronounced feature in the TR-PES spectra. A similar feature is observed for Ag_4O_2^- and Ag_8O_2^- , indicating the existence of an analogous desorption process. For Ag_3O_2^- we observe a rather long-lived excited state in agreement with the considerations mentioned above, i.e. the first system of reacted clusters (Ag_n^- clusters reacted with O_2) with rather long-lived excited states is identified. Our findings indicate that in this case oxygen is chemisorbed dissociatively and therefore desorption of O_2 is not possible. There might exist certainly more systems exhibiting long-lived excited states, which are expected to have interesting photochemical properties.

The experimental setup has been discussed in detail elsewhere [12]. Briefly, Ag_n cluster anions are synthesized using a pulsed arc cluster ion source (PACIS). Helium is used as carrier gas and a general valve with a backing pressure of 20 bar flushes the plasma into the extender. The trigger signals opening the valve have a duration of around 0.1 ms. The length of the water-cooled (~ 280 K) extender is 0.16 m and its diameter 4 mm. O_2 is introduced into the extender by a second valve, resulting in the effective generation of Ag_nO_2^- . In earlier studies oxygen was found to be mostly molecularly chemisorbed to even-numbered Ag cluster anions [13,14]. Not only even-numbered but also odd-numbered clusters can react with atomic oxygen, but for the odd numbered species dissociative chemisorption of oxygen is more likely. The anions are mass-selected using time-of-flight mass spectrometry. After mass-selection, the clusters are irradiated by two laser pulses ($h\nu_{\text{pump}} = 3.1$ eV, $h\nu_{\text{probe}} = 1.55$ eV) generated by a femtosecond laser system. The time resolution of the setup is better than 110 fs.

Photons of 3.1 eV are appropriate for photoexcitation of Ag_nO_2^- , whereas 1.55 eV photons do not lead to an excited state. Although the probe energy of 1.55 eV is rather low it has one crucial advantage: There were practically no two-photon processes even at high photon flux. The Ag_nO_2^- clusters have an excited state at 3.1 eV and two-photon processes were rather likely at this photon energy. At slightly increased photon flux, electrons from such two-photon processes conceal the weak pump-probe signal.

Thus, in a 3.1 eV/3.1 eV pump-probe experiment both pulses need to have a minimum photon flux resulting in an extremely weak pump-probe signal. With the intense 1.55 eV probe pulse, excited states and systems with low-electron affinities are easily detected. Therefore, this arrangement using strong but low photon energy probe pulses is especially suitable to study the time evolution of the excited states [15].

Fig. 1 displays a mass spectrum of Ag_n^- clusters reacted with O_2 molecules. An even-odd alternation of the reactivity can be observed: The even numbered clusters Ag_2^- , Ag_4^- , Ag_8^- , Ag_{10}^- and Ag_{12}^- almost completely react with O_2 , while Ag_3^- , Ag_7^- and Ag_9^- are inert (Ag_5^- and Ag_6^- have too low intensities and are not discussed). It was concluded that oxygen was molecularly adsorbed, since the electron affinity of the oxidized clusters compared to the respective bare ones increased only moderately and for some of the clusters a fine structure in the PES spectra was observed, which could be assigned to the O–O stretching vibration [13]. If atomic oxygen is provided in the cluster source, all Ag_n^- react resulting in formation of clusters with various numbers of Ag and O atoms in a cluster (not shown), which might also yield species with dissociatively chemisorbed oxygen. It is noteworthy to mention that in a previous study of Ag_2O_2^- dissociative chemisorption was detected for a small fraction of the clusters, depending on the conditions in the cluster source [14]. In the current work the dynamics of the species with molecularly adsorbed oxygen was examined.

Before discussing the time-resolved photoelectron spectra it might be helpful to have a closer look at the ground state electronic structures of Ag_n^- and Ag_nO_2^- clusters. Fig. 2 compares standard photoelectron spectra of Ag_n^- and Ag_nO_2^- with $n = 2, 3, 4$ and 8 [5,6,13,14,16]. Adsorption of O_2 results in an increase of the electron affinity by about 0.5 eV–1.3 eV. Note that detachment with 1.55 eV

Fig. 1. Mass spectrum of Ag_n^- clusters reacted with molecular O_2 . Clusters with even number of Ag atoms n easily adsorb a single O_2 molecule (marked ' n ' + O_2). The odd-numbered clusters react weakly with O_2 (e.g., $\text{Ag}_3^- + \text{O}_2$) [13,14].

Fig. 2. Standard photoelectron spectra of bare Ag_n^- and reacted Ag_nO_2^- clusters. The photon energy is 4.66 eV. O_2 chemisorption results in an increase of the electron emission threshold by about 1 eV. The spectrum of Ag_3O_2^- has been obtained by reaction with atomic oxygen. The spectra agree well with earlier results [6,15]. For all species except Ag_2^- the emission threshold is beyond the probe photon energy of 1.55 eV.

photons is possible only for Ag_2^- . The electronic structure is different for each cluster, especially in case of the reacted clusters. It seems unlikely that these clusters have excited states with similar properties (energy, lifetime, Franck-Condon profile).

Using TR-PES we studied the evolution of the clusters after absorption of 3.1 eV photons. The main processes following the primary absorption are described below:

The time evolution of the system is monitored by recording photoelectron spectra with the 1.55 eV probe pulse and only the species with sufficiently low electron affinities can be observed with this low photon energy, which are mainly transient excited states of the Ag_nO_2^- clusters and Ag_2^- . For species with an electron affinity lower than 3.1 eV the pump pulse contributes to the electron signal by photodetachment, which is independent of the pump-probe delay (the time-independent part is subtracted from each spectrum). Also, some time-independent features from undesired multiphoton processes are subtracted.

Fig. 3 displays time-resolved photoelectron spectra of Ag_nO_2^- with $n = 2, 4$ and 8. In all three cases broad peaks with vibrational fine structures (arrows) are observed, with their intensity decreasing exponentially with time. We assign these peaks to excited states of the anions Ag_2O_2^- , Ag_4O_2^- and Ag_8O_2^- with lifetimes of <100 fs, 400 ± 50 fs and <100 fs, respectively. For Ag_2O_2^- and Ag_8O_2^- we can only give upper limits of the lifetimes due to the limited time resolution of our experiment. The vibrational frequencies are determined to be 170 ± 40 meV, 320 ± 40 meV and 240 ± 50 meV, respectively.

The assignment to excited states of the anions is based on a detailed analysis of the Ag_2O_2^- series [17]. At increasing pump-probe delays a peak at a kinetic energy of 0.6 eV appears, which is assigned to photodetachment from Ag_2^- . Analysis of the peak shows a change of its shape with delay time, which can be observed in an ensemble only for a direct process, whereas for a statistical process the ensemble average leads just to an increase of the feature. Moreover, the extremely short lifetime also supports our interpretation for direct photodesorption in contrast to thermal photodesorption. The latter has been observed for $\text{Au}_2(\text{CO})^-$, $\text{Pt}_2(\text{CO})_5^-$ and $\text{Pt}_2(\text{N}_2)^-$ [10,11].

Interestingly, the spectra of Ag_4O_2^- and Ag_8O_2^- are similar to those of Ag_2O_2^- . Although we cannot observe the products of the assumed desorption process (Ag_4^- and

Fig. 3. Time-resolved photoelectron spectra of even-numbered Ag_nO_2^- clusters with $n = 2, 4$ and 8. The anions are excited with a 3.1 eV photon and the spectra are recorded using 1.55 eV photon energy. The broad feature at zero delay is assigned to photodetachment from an excited state of the anions, which exponentially decays with a short lifetime (<100 fs for $n = 2, 8$ and 400 ± 50 fs for $n = 4$). The peak at 0.55 eV kinetic energy in the series of Ag_2O_2^- is assigned to photoemission from ground state Ag_2^- . The arrows mark finestructures assigned to excitation of the O_2 stretching vibration.

Ag_8^-) due to their high electron affinities, the similarity of the peak shapes, peak positions and time evolution suggest that the underlying mechanisms of these three clusters should be analogous. We tentatively assign the observed broad maxima to excited states, which are localized close to the chemisorbed O_2 molecule and have an antibonding character, resulting in fast and direct desorption. The states are suggested to be localized because the electronic structure of the entire cluster varies strongly with increasing number of Ag atoms, yet the excited state changes only slightly.

In photoelectron spectroscopy, vibrational fine structure most likely corresponds to the structure of the final state of the photoionization, which is the neutral species in our case. For neutral Ag_2O_2 , the binding energy of the O_2 molecule is predicted to be low and a vibrational frequency close to the value of free O_2 is expected (195 meV), in line with our observation (170 ± 40 meV). For Ag_4O_2 and Ag_8O_2 , vibrational frequencies (300 meV and 240 meV, respectively) are larger, which are comparable or even higher than the one of the positive ion O_2^+ [18]. This result can partially be explained by charge transfer to the metal cluster. However, one should note that after this two-step photodetachment process involving two-photons, the neutral Ag_nO_2 cluster may not necessarily be in the electronic ground state, and there exist excited states of neutral O_2 with vibrational frequencies as high as 370 meV [18]. A detailed assignment is difficult in the present state of knowledge; however, in all three cases the vibrational fine structure can only be assigned to the O_2 stretching vibration. The broad Frank–Condon profile indicates that the state is indeed localized close to the oxygen molecule.

For Ag_2O_2^- this state decays by direct photodesorption indicating an antibonding character with respect to the O_2 –Ag bond [17]. Since all even-numbered clusters studied here exhibit excited states with similar energetic positions and vibrational fine structures, it seems likely that direct O_2 desorption also takes place in Ag_4O_2^- and Ag_8O_2^- .

In the case of Ag_3O_2^- theoretical studies predict for the geometrical structure a linear Ag_3 subunit with molecularly bound O_2 [19,20]. It is important to note that in these calculations the adsorption of molecular oxygen was investigated, but in our case atomic oxygen was provided for generating Ag_3O_2^- . This might lead to the creation of an isomer with dissociatively bound O_2 , which can be generated in large amounts using our source. Fig. 4 displays a series of TR-PES of Ag_3O_2^- , showing a single narrow peak (corresponding to an excited state) with a long lifetime of 5.4 ± 1.5 ps. Furthermore, no vibrational fine structure could be detected, which is also in contrast to the even-numbered clusters. These observations indicate a different dynamics after photoexcitation. If we assume dissociatively chemisorbed oxygen, direct desorption of O_2 is not possible, hampering the relaxation and leading to the observed long-lived excited state. The decay mechanism of this state cannot be revealed, using our present experimental setup.

Fig. 4. Time-resolved photoelectron spectra of Ag_3O_2^- . The clusters were generated using atomic oxygen. The narrow feature is assigned to photodetachment from an excited state of the Ag_3O_2^- anion. The lifetime for the excited state is 5.4 ± 1.5 ps.

In conclusion, we discovered excited states of Ag_nO_2^- clusters with even $n = 2, 4$, and 8 with high photoabsorption cross sections for a pump pulse energy of 3.1 eV. Excited states of these three different clusters are analogous, although the electronic structure varies strongly with increasing number of Ag atoms in the cluster. The state is localized close to the oxygen molecule and decays for Ag_2O_2^- into Ag_2^- and O_2 via direct photoinduced desorption. The states with similar energy, lifetime and vibrational fine structure found for Ag_4O_2^- and Ag_8O_2^- suggest similar direct photodesorption processes occurring for these clusters. On metal surfaces direct desorption is unlikely, because any excited state is quenched effectively by the high density of states (DOS) at the Fermi energy. In clusters the DOS is low, allowing longer lifetimes and/or competing processes become more likely. Our interpretation is supported by the finding of an excited state with a long lifetime for Ag_3O_2^- . Here, O_2 is suggested to be dissociatively chemisorbed and the only remaining fast decay channel (desorption) is blocked. The lifetime increases by more than one order of magnitude. For such small metal clusters, photoactivation and photodesorption may become dominant making these species interesting for photochemistry.

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