O$_2$ photodesorption from AuO$_2^-$ and Au$_2$O$_2^-$

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Abstract Using time-resolved photoelectron spectroscopy, the decay channels of AuO$_2^-$ and Au$_2$O$_2^-$ following photoexcitation with 3.1-eV photons have been studied. For AuO$_2^-$, a state with a rather long lifetime of 30 ps has been identified. Its decay path could not be determined but photodesorption can be excluded. For Au$_2$O$_2^-$, the spectra indicate O$_2$ desorption after 3.1-eV photoexcitation on a time scale of 1 ps. While comparing these results on Au$_n$O$_2^-$ with analogous data on Ag$_n$O$_2^-$ clusters, a discernible pattern emerges: for dissociatively bound O$_2$(AuO$_2^-$, Ag$_3$O$_2^-$), there are long-living excited states which do *not* decay by oxygen desorption, while for molecular chemisorption (Au$_2$O$_2^-$, Ag$_2$O$_2^-$, Ag$_4$O$_2^-$, Ag$_8$O$_2^-$), the 3.1-eV photoexcitation triggers fast O$_2$ desorption with a high quantum yield.

1 Introduction

Small metal clusters might be valuable building blocks of future photochemical devices suitable for, e.g., fuel production directly from sunlight. Metal clusters, especially the ones of the monovalent metals such as the alkali metals, silver and gold, interact strongly with light due to their collective valence-electron excitations [1, 2]. This makes them ideal light-harvesting antennas. The question arises how the energy of a photon is further processed in the cluster, especially if some adsorbate molecules are present on the surface

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of the particle. On metal surfaces, there is an overwhelming probability for thermalization of the photon energy, because excited states are efficiently quenched by the conduction electrons [3, 4]. Thus, if any photodesorption is observed at all, it occurs with a low probability and only due to indirect processes induced by hot electrons or hot phonons present in the vicinity of the adsorbed molecule [3]. But, thermalization and a low quantum yield are properties unfavorable for applications in energy conversion and photochemistry.

First studies on photochemistry of small metal clusters yielded the same result. Even small transition-metal clusters such as Ni$_3^-$ seem to have a sufficiently high density of electronic states and an excited state is quenched fast [5]. For Au$_2$(CO)$^-$, ultra-fast thermalization is dominant [6], which is surprising, since the density of electronic states of the Au$_2$ dimer is low [1] and quenching via Auger-like processes is unlikely. However, there is another fast relaxation mechanism for systems with a less rigid geometry: internal conversion [7, 8]. Here, photoexcitation triggers a fast geometry change and the system can approach the ground state potential surface through, e.g., a conical intersection, on a time scale of 100 fs. This has an effect similar to the quenching by the conduction electrons in a metal: the energy is thermalized very efficiently suppressing other processes such as desorption.

Recently, we started a systematic search for long-living excited states of metal clusters reacted with O$_2$ [9, 10] using time-resolved photoelectron spectroscopy (TRPES). We began with Ag and Au clusters reacted with oxygen, because oxides might have a more rigid geometric structure suppressing thermalization by internal conversion [7]. In addition, the metal cores have a low density of states at energies close to the highest occupied molecular orbital even for larger clusters such as Au$_{20}$ [11]. In the case of Ag$_n$O$_2^-$ clusters, we found an excited state with a lifetime of ∼5 ps

for $Ag_3O_2^-$ [10]. It was not possible to determine the decay channel of this long-living state, but oxygen desorption and fragmentation could be ruled out. Fast O_2 photodesorption was the main decay channel for even-numbered $Ag_nO_2^-$ clusters with $n = 2, 4$ and 8 [9, 10]. Unfortunately, in these earlier studies we lacked the higher probe photon energy necessary to expand these studies to $Au_nO_2^-$ clusters. Because of the surprising catalytic properties of small Au clusters, such photodesorption studies would be interesting [12]. However, oxidized and bare Au cluster anions have high electron affinities [1] and a relatively high photon energy of the probe pulse is necessary to conduct time-resolved photoemission experiments.

Here, we present first results using a photon energy of 4.65 eV (third harmonic of a Ti:sapphire laser) for the probe pulse to study the 3.1-eV photoexcitation of the two smallest $Au_nO_2^-$ anions with $n = 1$ and 2. For AuO_2^-, the data indicate the existence of an excited state with a rather long lifetime of $\sim$30 ps with no detectable subsequent fragmentation or desorption. For $Au_2O_2^-$, O_2 desorption is observed. The data can be compared to the ones of the silver species: $Ag_3O_2^-$ [10] and AuO_2^- behave similarly, and in both cases the two O atoms are probably bound dissociatively [13, 14]. The spectra of $Au_2O_2^-$, although with a poor signal to noise ratio, exhibit certain similarities to the ones of $Ag_2O_2^-$ [9], where our TRPES data indicate a direct desorption process. By comparison of all available results a discernable pattern emerges: for Ag and Au clusters reacted with oxygen internal conversion is slow, probably because of the more rigid structure. Around 3-eV excitation energy states of the $Ag_nO_2^-$ and $Au_nO_2^-$ clusters exist, that decay by direct desorption in the case of molecularly bound O_2, whereas for dissociatively bound O_2 desorption is either not possible or slow and the excited states have rather long lifetimes. However, the database of this picture is small yet and further studies are necessary. In the future, we will extend these experiments to larger cluster sizes determining up to which maximum size the pattern continues. Beyond a certain cluster size all such size effects should vanish due the overwhelming quenching efficiency of the increasing density of conduction electrons.

2 Experimental setup

The experimental setup has been described in detail elsewhere [9, 10]. Gold cluster anions are generated in a pulsed arc cluster ion source (PACIS) and O_2 is introduced into the source to generate $Au_nO_m^-$ clusters. The cluster anions are mass selected using a reflectron-type time-of-flight mass spectrometer. The bunch of cluster anions is irradiated by two laser pulses (pump and probe) with variable delay. The pump pulse is the second harmonic of a Ti:sapphire femtosecond (fs) laser system (400 nm = 3.1 eV) and the probe
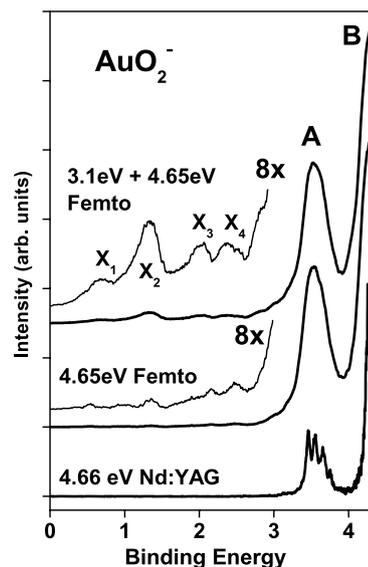

Fig. 1 Photoelectron spectra of AuO_2^-: *Upper trace:* TRPES at 7-ps delay with a photon energy of 3.1 eV and 4.65 eV of the pump and probe pulses, respectively. The features marked X_1–X_4 are assigned to an excited state of AuO_2^-. *Middle trace:* same spectrum as in the upper trace, but recorded with the probe pulse only. The small peaks visible at binding energies lower than 3 eV are produced by (unwanted) two-photon processes involving two 4.65-eV photons. *Lower trace:* reference spectrum obtained with a standard Nd:YAG laser pulse with a photon energy of 4.66 eV

pulse is the third harmonic (4.65 eV). The time resolution of the setup is better than 250 fs. The kinetic energy of the detached electrons is measured using a 'magnetic bottle' type time-of-flight electron spectrometer, operated at a moderate energy resolution of 100 meV. The temperature of the cluster anions is estimated to be roughly room temperature, since the anions spend a sufficient amount of time inside the water-cooled extender (4-mm diameter, 20-cm long), to allow for thermalization. Great care has been taken to optimize the pulse energies of the 3.1-eV pulse (the pump pulse) to a value just below the onset of two-photon processes (i.e. two-photon processes induced by the pump pulse only). The pulse energy of the 4.65-eV pulse is relatively low. Therefore, it is set to the maximum value the laser system is able to provide. Photoelectrons can be detected from all anions with electron affinities lower than the photon energy. From any neutral fragments no signals can be detected due to the high ionization potentials.

3 Results and discussion

3.1 AuO_2^-

The upper trace in Fig. 1 displays a time-resolved photoelectron spectrum of AuO_2^- recorded at 7-ps delay between the two pulses. The two features marked A and B are assigned

to photodetachment from the electronic ground state and agree nicely with the reference ground state spectrum obtained with a 4.66-eV pulse of a Nd:YAG laser (lower trace). The only difference is the lower energy resolution we obtain for the time-resolved spectra, which is partly due to the energy width of the femtosecond pulse and partly due to the high-intensity mode of operation of the electron spectrometer. Feature A shows a pronounced vibrational fine structure and corresponds to the transition from the ground state of the anion into the neutral ground state. From the vibrational fine structure it can be concluded that O_2 is bound dissociatively [14]. Feature B is assigned to the transition into the first excited state of neutral AuO_2.

The spectrum at 7-ps delay exhibits additional peaks (marked X_1–X_4), which we tentatively assign to transitions from an excited state of the anion AuO_2^- into the ground and excited states of the neutral cluster. Peak X_1 corresponds to the transition into the neutral ground state and X_2 to the one into the first excited state. The energy separation between X_1 and X_2 corresponds to the spacing between A and B, supporting this assignment. In addition, the energy difference between X_1 and A matches almost exactly the photon energy of the pump pulse (3.1 eV). Thus, the four peaks X_1–X_4 can be assigned to photoemission from an excited state of AuO_2^-. If the pump–probe delay is increased further the intensities of the excited-state features decrease. Figure 2 shows a series of TRPES spectra recorded at variable pump–probe delays. The spectra are difference spectra displaying the time-dependent signal only. At delays beyond 40 ps the excited-state signal vanishes. From this series the lifetime of the excited state is determined to be 30 ± 10 ps. The shape and binding energies of the excited state peaks do not vary with time within the accuracy of our experiment; only the intensity decreases. This behavior has been found for several small clusters in the past (Ag_3^- [8], Au_6^- [15]) and is similar to the case of an excited state of an atom.

Although the spectra displayed in Figs. 1 and 2 show that the excited state of AuO_2^- decays with a certain lifetime, the data do not provide a clue about the decay channel. Fragmentation or desorption should result in the appearance of features in the spectra assigned to Au^-, O^- or O_2^-. However, no such signals could be detected. Another decay channel is internal conversion [7], producing hot anions in their electronic ground state. Photoemission from such hot anions should result in spectra which are basically similar to the ground-state spectra (middle trace in Fig. 1), but the two main peaks A and B should be broadened. Only a fraction of anions is excited by the pump pulse. The signal from such 'hot' ground-state anions is always superimposed on the dominant emission from anions which have not been excited. We did such an analysis and there is a broadening, but it is small considering the huge energy (3.1 eV) stored in the excited anions. Therefore, our data do not support thermalization being the decay channel. Another decay channel is
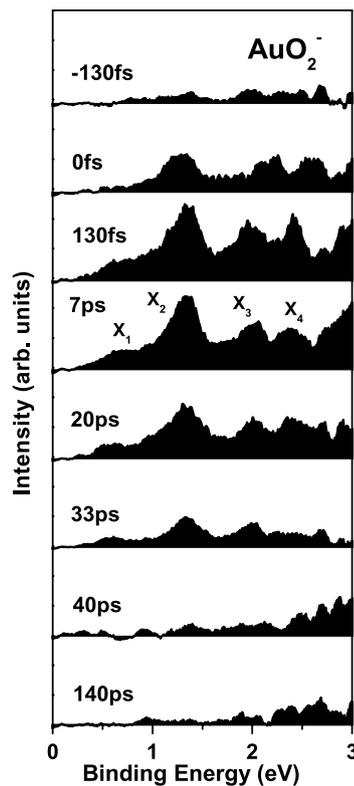

Fig. 2 Series of time-resolved photoelectron spectra of AuO_2^- recorded at various pump–probe delays. The spectra are difference spectra displaying the time-dependent signal only. The photon energy of the pump pulse is 3.1 eV and the one of the probe pulse is 4.65 eV. The excited-state peaks X_1–X_4 vanish at delays beyond 40 ps. The lifetime of the state is determined to be 30 ± 10 ps

vibrational autodetachment [16], which becomes possible if the excitation energy (3.1 eV) is close to the electron affinity. The process can be explained within the single-particle picture. The electron is excited just below the binding energy into a weakly bound state. Then, a small amount of additional energy from the vibrational modes of the cluster is sufficient to detach the electron. The adiabatic electron affinity of $Au_1O_2^-$ is unknown, but it is smaller than 3.4 eV and above 2.9 eV, according to our data. Therefore, this process could take place in this system. It would create electrons with low kinetic energies (0–200 meV), which we cannot observe with our spectrometer, because its minimum passing energy is 200 meV. Thus, based on our data alone, we cannot determine the decay channel of the excited state of AuO_2^-.

3.2 $Au_2O_2^-$

In contrast to the case of the monomer, for $Au_2O_2^-$ we observe a pattern indicating O_2 photodesorption. Figure 3 displays time-resolved photoelectron spectra recorded at zero (top trace) and long (second top trace) pump–probe delays. The lower two traces show a comparison with the standard
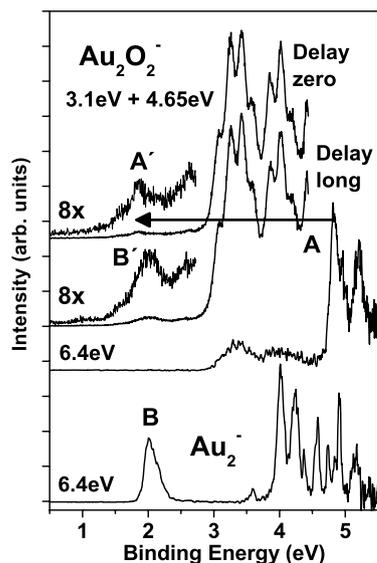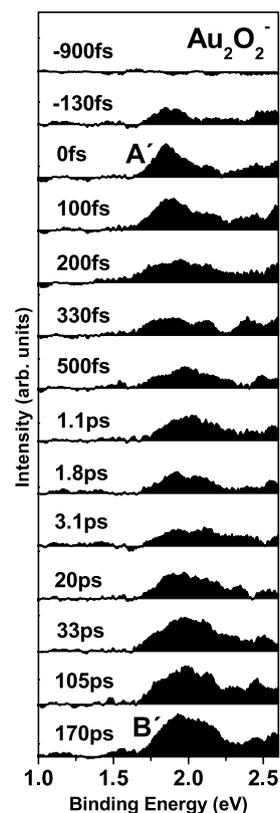
Fig. 3 Time-resolved photoelectron spectra of $Au_2O_2^-$ recorded at zero (*top trace*) and long (*second top trace*) pump–probe delays. The trace at long delays has been obtained by adding up spectra recorded at 33 ps, 40 ps, 72 ps, 140 ps and 172 ps, improving the signal to noise ratio. The photon energy of the pump pulse is 3.1 eV and the one of the probe pulse is 4.65 eV. The *lower two traces* display reference spectra of $Au_2O_2^-$ and Au_2^-, respectively, recorded with an excimer laser operated at a photon energy of 6.4 eV (ArF). The *arrow* indicates the presumed excitation of $Au_2O_2^-$ due to the absorption of a photon of a pump pulse. For a discussion of the marked features, see text

Fig. 4 Series of time-resolved photoelectron spectra of $Au_2O_2^-$ recorded at various pump–probe delays. The photon energy of the pump pulse is 3.1 eV and the one of the probe pulse is 4.65 eV. The traces are difference spectra displaying the delay-dependent part of the signal only. Only the low binding energy regime is displayed. The two features marked A′ and B′ are the same as in Fig. 3. The relatively narrow peak A′ can be observed at delays very close to zero only and broadens almost immediately. On a time scale of several tens of ps a broad peak B′ grows, which is located at slightly higher binding energy than A′. The total intensity of the pump–probe signal (*blackened area*) decreases by ~30% and reaches a minimum at 1.8 ps. With further increasing delay the intensity increases again and exceeds the one at zero delay by ~ 25% at long delays

ground-state spectra of $Au_2O_2^-$ and Au_2^- recorded at 6.4-eV photon energy. At long pump–probe delay, a broad feature (marked B′) appears at a binding energy of ~2 eV. Within the accuracy of our experiment, it is located at the same binding energy as the corresponding feature in the spectrum of Au_2^- (marked B). Accordingly, we assign the peak B′ to Au_2^- being a product of O_2 photodesorption from $Au_2O_2^-$. The fragment feature B′ is considerably broader than the ground-state peak B of Au_2^-. This is to be expected, because after photodesorption some excess energy will remain in the metal cluster resulting in an enhanced vibrational temperature. Peak A′ observed at zero delay (Fig. 3, top trace) can be assigned to an excited state of $Au_2O_2^-$, which then decays by desorption. Analogous to the case of AuO_2^-, it is possible to assign the excited-state peaks to ground-state peaks shifted by the excitation energy of 3.1 eV. The ground-state spectrum of $Au_2O_2^-$ recorded at 6.4-eV photon energy (Fig. 3, next to bottom trace) is dominated by an intense peak (marked A) at a binding energy of 4.8 eV, which nicely corresponds to excited-state feature A′ at a binding energy of 1.8 eV.[1] The presumed excitation is indicated by the horizontal arrow.

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[1] The difference in binding energy is not necessarily exactly equal to the photon energy, because each peak corresponds to a different electronic transition with an individual Frank–Condon profile.

With increasing pump–probe delay, the zero-delay spectrum (Fig. 3, top trace) should gradually evolve into the spectrum recorded at long delays. This corresponds to a transformation of peak A′ into peak B′. Analogous to the case of $Ag_2O_2^-$ [9], we assigned peak A′ observed at zero delay to the excited state and peak B′ to the photodesorption product Au_2^-. At intermediate pump–probe delays, it should be possible to observe the desorption 'online' via changes of the electronic structure. Figure 4 displays the results of our efforts to examine this transition region. At zero delay a relatively narrow peak A′ is observed, which develops into a broad feature within 100–200 fs. The total intensity of the pump–probe signal decreases by ~30% and reaches a minimum around 1.8 ps. Such a signal decrease indicates a change of the electronic structure altering the detachment cross section. With further increasing delay a broad peak marked B′ develops. Its intensity increases gradually until it stabilizes at delays beyond 100 ps.

We assign this series of pump–probe spectra to a direct photodesorption process of O_2 from the $Au_2O_2^-$ cluster. The series of time-resolved photoelectron spectra agree with the following picture: the 3.1-eV photon excites $Au_2O_2^-$ into an antibonding state, which gives rise to the relatively narrow peak at zero delay (Fig. 4: 0-fs trace, marked A′). The system develops downhill on the excited state potential surface

(the Menzel–Gomer–Redhead scenario [17, 18]) and the corresponding peak in the photoelectron spectrum broadens and shifts towards higher binding energy (Fig. 4: 500-fs and 1.1-ps traces). The integrated intensity (blackened area in Fig. 4) decreases by ∼30% after 1.8 ps, indicating a change of the cross section due to the altered electronic structure during desorption. Finally, the neutral O_2 detaches from the metal core and the spectrum develops into the one of the ground state of Au_2^- (Fig. 4: 1.8-ps to 170-ps traces). It takes a surprisingly long time until the Au_2^- ground-state peak (Fig. 4, marked B′) gains its maximum intensity. The integrated pump–probe signal is now higher by 25% compared to the one at zero delay, indicating another change of the electronic structure. The slow intensity increase on a time scale of roughly 30 ps can be explained by the assumption that O_2 desorbs slowly with low kinetic energy.

This is a tentative picture only and needs further support by corresponding calculations, which are not available at present. But, the sequence of pump–probe spectra displayed in Fig. 4 suggests that the process is direct. The data are not consistent with a statistical process as in the case of $Au_2(CO)^-$ [6]. In a statistical process, the excited-state peak decreases in intensity while simultaneously the fragment peak grows. Here, the excited-state peak A′ shifts and broadens and finally the fragment peak B′ appears. The observed minimum of the integrated intensity is also not consistent with thermal desorption, because in that case the intensity is expected to change gradually from the one of the initial state to the one of the final state with no minimum or maximum in between.

4 Comparison with $Ag_nO_2^-$ clusters and metal surfaces

Our data on AuO_2^- and $Au_2O_2^-$ taken alone do not allow an unambiguous assignment to certain processes because of limited time resolution and signal to noise ratio. However, a comparison with analogous data on $Ag_nO_2^-$ clusters [10] suggests an intriguing explanation of our findings.

First of all, it seems that oxides of the Ag and Au clusters exhibit less effective relaxation by internal conversion. This is a prerequisite for the existence of long-living excited states with lifetimes above 500 fs. In addition, the density of states is low enough to reduce quenching of electronically excited states by Auger-like processes, which is by far the dominating process on metal surfaces [3, 4]. Hence, for these clusters the usual relaxation channels are blocked or slowed down. But, what is now the dominant decay pathway of the excited states? Based on the studies we conducted so far, we can distinguish between two groups:

4.1 First group

O_2 is dissociatively bound. This is the case for AuO_2^- and $Ag_3O_2^-$ [10].[2] For both examples we observe excited states with a lifetime of several picoseconds. Here, the direct decay channel of O_2 desorption is not open, and other decay channels are slow. The decay paths of $Ag_3O_2^-$ and AuO_2^- are not known yet, but desorption and fragmentation can be excluded.

4.2 Second group

O_2 is molecularly bound. This is the case for many even-numbered $Ag_nO_2^-$ and $Au_nO_2^-$ clusters [14, 19]. For these species we observe ultra-fast photodesorption on a time scale of less than 500 fs. Absorption of a 3.1-eV photon excites the system into an antibonding state. If this interpretation of our data is correct, the excitation in clusters proceeds as predicted by the Menzel–Gomer–Redhead model developed for surfaces [17, 18], but with almost no competing relaxation and high quantum yield. The examples $Ag_2O_2^-$, $Ag_4O_2^-$, $Ag_8O_2^-$ and $Au_2O_2^-$ fit well into this picture.

5 Conclusion

We studied the 3-eV photoexcitation of AuO_2^- and $Au_2O_2^-$ using time-resolved photoelectron spectroscopy of mass-selected anions. AuO_2^- exhibits a rather long-living excited state with a lifetime of 30 ps. The long lifetime indicates that the usual relaxation processes such as internal conversion or relaxation by electron–electron interaction (Auger-like processes) are slow. The excited state does not decay by desorption or fragmentation. For $Au_2O_2^-$, a different behavior is found: the 3.1-eV excitation results in fast desorption of the O_2. An analogous behavior has been found for $Ag_nO_2^-$ clusters. Taking all data we recorded so far on the $Ag_nO_2^-$ and $Au_nO_2^-$ clusters into consideration, a pattern emerges:

If the oxygen is bound dissociatively, excited states with rather long lifetimes exist, while for species with molecularly bound O_2 the 3.1-eV excitation triggers immediate photodesorption. Both mechanisms are not observed for metal surfaces and make the clusters interesting candidates for future applications in photochemistry.

[2]For AgO_2^- we were not able to record a pump–probe signal. This is probably due to the fact that this cluster has no excited state around 3.1-eV excitation energy.

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