

O₂ photodesorption from a Ag₈O₂⁻ cluster

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Abstract. The decay path of an Ag₈(O₂)⁻ cluster photoexcited by a 3.1 eV photon is elucidated using time-resolved photoelectron spectroscopy. Photoabsorption results in the formation of an excited state giving rise to a peak in the photoelectron spectra with well-resolved vibrational finestructure. With a lifetime of about 100 fs this bound state decays into an anti-bonding state which dissociates into O₂ and Ag₈⁻ on a timescale of 10 ps. In the photoelectron spectra, this corresponds to a broad maximum shifting gradually towards higher binding energy while the O₂ and Ag₈⁻ separate. Finally, the spectrum of bare Ag₈⁻ appears. This process is unique to small clusters, because on metal surfaces excited state lifetimes are too short to allow for direct dissociation.

PACS. 68.43.Tj Photon stimulated desorption – 78.47.J- Ultrafast pump/probe spectroscopy – 33.80.Eh Autoionization, photoionization, and photodetachment – 36.40.-c Atomic and molecular clusters

Photochemical properties of small metal nanoparticles and metal clusters might be different from the ones of the corresponding bulk surfaces [1]. One property of metal surfaces is the low photodesorption quantum yield for direct processes ($<10^{-3}$) [2–4]. In case of direct desorption, the system propagates on the anti-bonding excited state surface downhill with the molecule detaching from the surface. In contrast, on metal surfaces thermal desorption prevails. Any excited state is quenched within a few femtoseconds by the strong interaction with the conduction electrons. Lifetimes are too short and excited states relax into the ground state before desorption takes place [4]. Therefore, at low light intensities (single photon processes) the quantum yield is low. At higher light intensities multiple excitations [5] or indirect processes involving hot conduction electrons or phonons drive desorption [3,4]. In metal clusters [6] the situation can be different. There are few “conduction” electrons (i.e., delocalized valence electrons) only and the density of states is small and this could slow down energy dissipation. The lifetime of an excited state might be long enough to allow the system to evolve on the excited state potential surface as proposed in one of the first and most simple model of photodesorption proposed by Menzel and Gomer [7] and Redhead [8] in 1964. In this case, the quantum yield is close to 100%. Here, we present new results from our efforts to find at least one metal cluster and molecule system which exhibits such a behavior.

So far, there are no systematic experiments comparing photodesorption from metal clusters with the one from metal surfaces. For metal surfaces, fast relaxation hampers desorption. After photoexcitation, the molecule starts moving on the excited state surface towards desorption. This process is stopped by the ultrafast relaxation back into the ground state and the molecule has not enough time to desorb [2]. There is one time-resolved experiment supporting this picture. Photoexcitation of a Cs atom adsorbed to a Cu(111) surface results in the elongation of the bond [9], but relaxation stops desorption and the Cs atom does not desorb. To our best knowledge time-resolved experiments on metal surfaces [3,4] and metal nanoparticles [1] were not yet successful in observing the breaking of the bond during photodesorption. Using pump-probe techniques this is difficult for processes initiated by hot electrons or phonons because of their statistical nature. As for thermal desorption, each molecule desorbs at a different time incoherent with the excitation event.

For direct desorption a long-living excited state is necessary. There was a search for such states in bare metal clusters using time-resolved photoelectron spectroscopy (TRPES) [10,11]. However, even for the smallest clusters with three metal atoms only very short lifetimes have been found. There are two explanations for this surprising finding:

- for clusters of open *d*-shell clusters such as Ni₃ [10] the density of states close to the HOMO might be sufficiently high to enable bulk-like fast relaxation.

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- another relaxation process is internal conversion, which can be fast in clusters with a fluxional geometry such as Al_{13} [11].

In these cases photodesorption proved to be thermal and not much different from the behavior found for metal surfaces [12,13]. It is important to note that discrimination between direct and thermal desorption is straight forward in TRPES experiments: in a direct process the excited state feature is expected to shift towards lower binding energy, while for a thermal process the product peak gradually increases in intensity as observed for $\text{Au}_2(\text{CO})^-$ [12].

For clusters of simple metals such as Ag the situation is different. They have a low density of states and long-living excited states have been detected for neutral Ag_8 [14] and for the anion Ag_8^- [15]. Hence, this cluster is a promising candidate for a search for direct photodesorption processes in metal clusters. It is known that for the even-numbered Ag_n^- clusters O_2 is bound molecularly being a prerequisite for direct desorption [16]. Furthermore, in a previous TRPES experiment on the oxidized dimer $\text{Ag}_2^-(\text{O}_2)$ we found indications for the existence of a direct photodesorption process [17]. However, there the process was too fast and we could not reveal details. We also examined $\text{Ag}_4^-(\text{O}_2)$ and $\text{Ag}_8^-(\text{O}_2)$, but at that time the probe photon energy (1.55 eV) was too low to allow for a detailed analysis of the decay path after excitation [18].

Here, we present TRPES data on $\text{Ag}_8(\text{O}_2)^-$ using a higher probe photon energy (4.65 eV). Now it is possible to observe the time evolution after photoexcitation until the system reaches its final state. Absorption of a 3.1 eV photon results in the excitation of a bound excited state corresponding to a peak in the photoelectron spectrum with a well-resolved vibrational finestructure. This state decays within 100 fs into an anti-bonding state giving rise to a broad feature in the spectrum. The broad feature shifts towards higher binding energy directly mirroring the desorption process. Finally, the feature develops into a peak well-known for bare Ag_8^- . Hence, we found what we were looking for: a direct photodesorption process, which is not likely to occur on metal surfaces and is unique to clusters.

The experimental set-up has been described in detail elsewhere [15,17,18]. Silver cluster anions are generated in a pulsed arc cluster ion source (PACIS) and O_2 is introduced into the source to produce Ag_nO_m^- clusters. The cluster anions are mass-selected using a time-of-flight mass spectrometer. A bunch of Ag_8O_2^- anions is irradiated by two laser pulses (pump and probe) with variable delay, the pump pulse being the second harmonics of a Ti:sapphire femtosecond (fs) laser system ($400 \text{ nm} \hat{=} 3.1 \text{ eV}$) and the probe pulse being the third harmonics ($267 \text{ nm} \hat{=} 4.65 \text{ eV}$). Due to the low conversion efficiency the pulse energy of the probe pulse is low ($<10 \mu\text{J}$) making the experiment rather time consuming. The time-resolution is approximately 150 fs. The kinetic energy of the detached electrons is measured using a “magnetic bottle” type time-of-flight electron spectrometer, operated at moderate energy resolution of $\sim 100 \text{ meV}$. The temperature of the cluster anions is estimated to be room

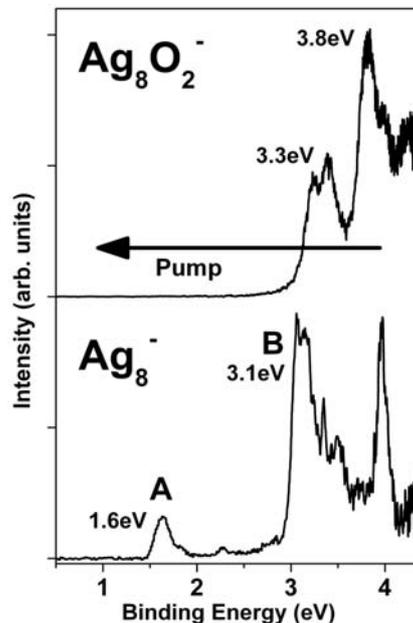


Fig. 1. Ground state photoelectron spectra of Ag_8O_2^- recorded with a photon energy of 4.65 eV (upper trace) [16] and of the bare metal cluster Ag_8^- recorded with a photon energy of 5 eV [19]. The binding energies of the relevant features are given in the figure. The arrow indicates the presumed pump excitation.

temperature. Great care has been taken to optimize the pulse energy of the pump pulse. It is optimized at long delays, maximizing the photofragment signal (Ag_8^-) and minimizing the two-photon signal from the pump pulse alone. The (low) pulse energy of the probe pulse corresponds to the maximum energy available, which is limited by the laser system and the conversion efficiency.

As reference, Figure 1 shows ground state photoelectron spectra of the parent cluster Ag_8O_2^- [16] and the bare metal cluster Ag_8^- [19]. Neutral Ag_8 is a magic cluster with a closed electronic shell, a large HOMO-LUMO gap and low density of states. The additional electron of the anion Ag_8^- is weakly bound (peak A in Fig. 1). All the small even-numbered Ag_n^- cluster anions adsorb O_2 easily because they have this weakly bound electron [16]. O_2 is molecularly chemisorbed and the bond is mainly formed by charge transfer from the metal cluster to the O_2 . Although this is a simple picture, it is sufficient for a qualitative understanding of our data. O_2 chemisorption to Ag_8^- results in the disappearance of peak A, now occupying an energetically more favorable $\text{O}_2\text{-Ag}_8$ hybrid orbital.

Figure 2 displays a series of pump-probe photoelectron spectra of $\text{Ag}_8(\text{O}_2)^-$ (pump: 3.1 eV/probe: 4.65 eV). The spectra are difference spectra, i.e. part (90%) of the delay independent signal has been subtracted for better clarity. The delay independent signal is mainly caused by single photon emission from the probe pulse and dominates the spectra above 3 eV binding energy (see upper trace in Fig. 1 for comparison). For delays 0 fs, 100 fs and 250 fs the spectra recorded previously [18] with the low

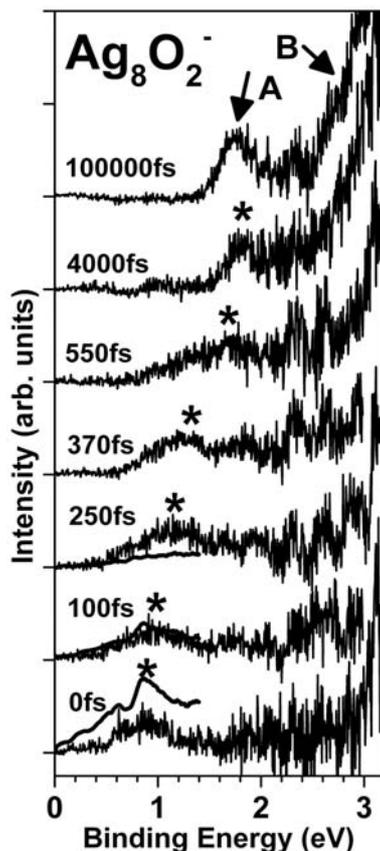


Fig. 2. Series of pump-probe difference spectra of Ag_8O_2^- . The photon energy of the pump pulse was 3.1 eV and the one of the probe pulse 4.65 eV. At zero delay a feature assigned to the excited state of Ag_8O_2^- appears and, with increasing delay, shifts towards higher binding energy (marked by asterisks). The trace at 370 fs delay is plotted up to 3 eV only for better visibility. Features A and B correspond to the peaks observed in the spectrum of bare Ag_8^- (lower trace in Fig. 1) and indicate complete O_2 photodesorption. For the delays 0 fs, 100 fs and 250 fs the spectra recorded previously [18] are included in the spectra (thick lines with low noise). For these data, the pump photon energy was the same, but the probe photon energy was 1.55 eV only. The intensity of the old data set is fitted to the new one at 100 fs delay.

probe photon energy (1.55 eV) are included in the spectra (thick lines with low noise). The range of these spectra extends up to 1.4 eV. This pump-probe signal decays with a lifetime of ~ 100 fs. The new data, although rather noisy due to the low probe laser intensity, agree with the old data and cover a broader energy range. At zero delay both traces agree about the vibrational finestructure, which can be assigned to the O_2 stretching vibration.

The two data sets disagree about the time dependence. While the 1.55 eV data show a fast decrease of the signal, the new data recorded with the higher probe photon energy (4.65 eV) do not show a clear indication of a reduction of the total pump-probe signal. Instead, a broad feature is visible which shifts gradually towards higher binding energy. After about 550 fs it reaches its maximum width

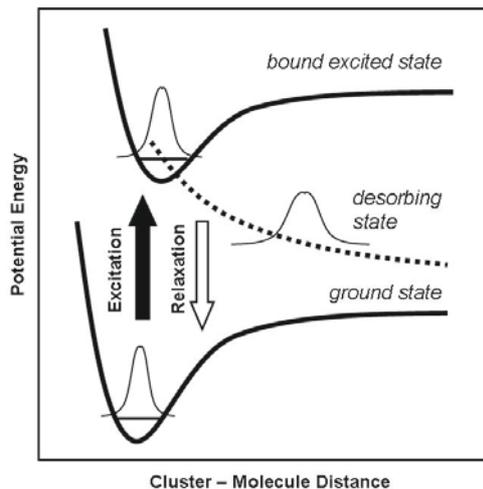


Fig. 3. Possible scenario explaining the TRPES data displayed in Figure 2. The first excitation goes into a bound state explaining its vibrational finestructure. This state has a larger detachment cross section at low photon energy and its signal dominates the 1.55 eV set of data. After about 100 fs it decays in an anti-bonding state and the photodesorption process starts. The downshift of the excitation energy corresponds to the increase in binding energy of the broad peak marked by asterisks in Figure 2.

covering the range from 0.8 eV to 2 eV centered at 1.6 eV. The approximate center of the broad feature is marked by asterisks illustrating the shift with increasing time. With time the feature eventually narrows down and stabilizes at long delays (beyond 4 ps) at 1.7 eV (marked A) with no further change. In addition, at high binding energy (2.5–3.2 eV) a shoulder appears at delays longer than 550 fs (marked B). These two features show a striking similarity to the two peaks marked A and B in the spectrum of bare Ag_8^- (Fig. 1, lower trace).

As obvious from Figure 2, the pump-probe data obtained with 3.1 eV/1.55 eV pulses indicate a lifetime of less than 100 fs, while the new data obtained with 3.1 eV/4.65 eV pulses just show a shifting peak with no signal loss. It looks as if two different excited states have been studied in the two experiments. Without calculations we can offer a tentative interpretation only. We think our observations can be explained best by the scenario illustrated in Figure 3. We believe that indeed two different excited states are involved. The first excitation goes into a bound state explaining the pronounced vibrational finestructure. The state might have a large detachment cross section at low photon energy, which is a common observation for orbitals with predominant s -character. This bound excited state decays quickly into an anti-bonding state with different symmetry. At high photon energy, detachment from the bound and presumably s -derived state has a low cross section and the spectra are predominated by the signal from the anti-bonding state.

With increasing time the O_2 starts to desorb and the electronic structure develops from the one of the excited state of $\text{Ag}_8(\text{O}_2)^-$ to the one of the ground state of Ag_8^- .

This development corresponds to a downhill movement on the potential surface of the desorbing state in Figure 3. The downhill movement means a decrease of the excited state energy and this is what the spectra in Figure 2 display: an increase of the binding energy of the excited state peak corresponding to a decrease of the excited state energy (asterisks in Fig. 2). As expected from Figure 3 and the Menzel, Gomer and Redhead picture [2], the feature broadens during desorption. At last, the chemisorption bond breaks and the spectrum gradually turns into the one of bare Ag_8^- . The most intriguing difference to the data on thermal photodesorption [12] is that the fragment peak of Ag_8^- does not gradually grow in intensity, but appears as a result of the shifting of the excited state feature.

There are two conclusions:

- **No ultrafast relaxation in $\text{Ag}_8(\text{O}_2)^-$.** In contrast to metal surfaces [2–4], there is no detectable relaxation competing with desorption in $\text{Ag}_8(\text{O}_2)^-$. This can be attributed to the low density of electronic states in the small nanocluster [6].
- **Direct observation of the bond breaking.** Our data display the anti-bonding excited state of the adsorbate-substrate complex, its course of development towards lower excitation energy and the final state, which is the ground state of the product. To our best knowledge, this breaking of the chemisorption bond has not been observed in a time-resolved experiment so far. Compared to experiments on surfaces, our set-up has one crucial advantage. For each laser shot a fresh sample consisting of an ensemble of $\text{Ag}_8(\text{O}_2)^-$ cluster anions is prepared. This is not possible on surfaces.

In conclusion, we studied the photodesorption of O_2 from Ag_8^- using time-resolved photoelectron spectroscopy. The data are tentatively explained with the following scenario involving two excited states: absorption of a 3.1 eV photon results in the excitation of the adsorbate-substrate complex into a bound excited state with a pronounced vibrational finestructure. Shortly after excitation, this state decays into an anti-bonding state and, while travelling downhill on the excited state potential surface, the O_2 desorbs. In the time-resolved spectra, the downhill movement is visible as a shift of the excited state peak towards

higher binding energy merging finally into the spectrum of bare Ag_8^- . On the time scale of desorption, no competing relaxation is observed in contrast to metal surfaces and larger nanoparticles.

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