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Photodesorption of O₂ from Ag₂⁻: A time-resolved study of Ag₂O₂⁻

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ABSTRACT We present time-resolved photoelectron spectra of mass-selected Ag₂O₂⁻ anions. The anions are photoexcited by photons with an energy of 3.1 eV, and photoelectron spectra of the excited species Ag₂O₂^{-*} and the subsequently appearing fragments are recorded using a probe laser pulse with a photon energy of 1.5 eV. The excited state of Ag₂O₂⁻ has a short lifetime of 130 fs ± 70 fs only and decays by direct photodesorption of O₂. The data demonstrate the ability of time-resolved photoelectron spectroscopy (TR-PES) to observe the breaking of chemical bonds if the decay process of the excited state is direct (non-thermal desorption). The data are compared to recent results of a NeNePo experiment [1] on the same system.

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1 Introduction

The interaction of photons and matter is of great interest in material science and chemistry, since absorption of photons can result in excitation of electrons, which may trigger various processes. When the photon energy is above the work function of a metal, the electron can leave the system as a free photoelectron, whereas for a photon energy smaller than the work function, the electron can be excited from occupied to unoccupied states and then relax via various mechanisms. In bulk metals, the most likely relaxation process is the dissipation of excess energy created by a single particle excitation among the free conduction electrons via Auger-like electron–electron interaction, in which the energy is thermalized within 10–100 femtoseconds (fs) [2, 3]. When the electron is excited into an antibonding state of an adsorbate on the surface, the excitation might also cause direct photodesorption of the adsorbate [4, 5]. For bulk metals, this process competes with the faster Auger-like relaxation [6].

In metal clusters the situation is different because the relaxation of single particle excitations by Auger-like processes could be suppressed due to the low density of electronic states [7, 8], similar to the case of a semiconductor surface [5]. As the major relaxation channel in bulk metals is suppressed in cluster systems, the quantum yield for photodesorption might be drastically enhanced. Absorption of a photon with an energy higher than the binding energy of the molecule can trigger a direct photodesorption process with a relatively high probability due to the lack of the competing relaxation channel.

So far, experimental results on cluster-adsorbate systems such as Pt₂N₂⁻ were found to be not in line with the general idea aforementioned [9, 10]. Even very small clusters of open d-shell metals like Pt₃⁻ or Ni₃⁻ show fast relaxations similar to bulk metals because of the high density of states even in such small systems [11–13]. Therefore, direct photodesorption can be considered to be as unlikely as in the case of bulk surfaces. However, the quantum

yield of photodesorption from clusters is still higher than in systems of the bulk counterparts, since dissipation of the photon energy results in a high vibrational temperature of the finite size system so that a molecule may desorb thermally [9, 10, 14]. In this case, the final state is the same as in case of direct photodesorption; however, the mechanism of thermal desorption is statistic, i.e., in an ensemble each system decays at a slightly different time described by a lifetime law.

Clusters of monovalent metals like Ag and Au have low densities of electronic states [15, 16] and electron–electron relaxation is not allowed or much slower than in the bulk [17]. Therefore, in such systems photodesorption of molecules chemisorbed to Ag_n or Au_n clusters (n = number of atoms) might be very efficient and occur in a direct process. However, the first study on such a system (Au₂(CO)⁻ [10]) revealed thermal desorption of CO instead of photo-induced direct desorption: Electronic excitation energy is first thermalized among the (few) vibrational degrees of freedom of the cluster and the high vibrational temperature then causes desorption of the CO molecule.

Here, we present data obtained using time-resolved photoelectron spectroscopy (TR-PES) for Ag₂O₂⁻. In this system photodesorption initiated by absorption of a photon with an energy of 3.1 eV occurs in a direct process. Such systems might be ideal candidates for observing the breaking of the chemical bond between metal and adsorbate and the subsequent reorganization of the electronic structure of the metal after desorption in real-time using TR-PES. Our data reveal that for Ag₂O₂⁻ photodesorption proceeds via an excited state

of Ag_2O_2^- with a short lifetime close to our experimental resolution (110 fs). Recently, photodesorption of the same system has been studied using NeNePo, in which the NeNePo data suggested a different desorption mechanism [1]. Various reaction pathways detected in our experiments using TR-PES and in the previous NeNePo studies will be discussed.

2 Experimental setup

The experimental setup has been described in detail elsewhere [18]. Briefly, Ag_n cluster anions are synthesized using a pulsed arc cluster ion source (PACIS). O_2 is introduced into the extender resulting in the effective generation of Ag_2O_2^- . From earlier photoelectron spectroscopy studies using a nanosecond pulse laser, oxygen was found to be mostly molecularly chemisorbed to Ag_2^- under such conditions [19]. 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. At the stage of TR-PES, the cluster temperature is estimated to be roughly room temperature. The time resolution and the time-zero are determined by plotting the intensity of a pump-probe feature of a selected cluster versus time-delay. The excited state of this selected cluster should have a lifetime much shorter than our time resolution. This plot corresponds to the “in-situ” autocorrelation function. For the present measurements, the TR-PES signal of a short-lived excited state of Ag_3^- is used for the laser pulse characterization. An upper limit of the time resolution of our experimental setup is determined to be 110 fs [20].

In our two color pump-probe experiments, an excitation energy of 1.55 eV is not sufficient to initiate photodesorption of oxygen from Ag_2O_2^- ; hence, the pulse with a photon energy of 3.1 eV should be used as pump pulse. In the present setup, we could only record the photoelectron spectra of the optically excited states using a probe pulse with a photon energy of 1.55 eV. Among various fragments induced by the pump photon, only those species with electron affinities or ionization potentials (IP) lower than 1.55 eV can be detected

in our experiment. Neutral photofragments with high ionization potentials (e.g. O_2 : IP of 12.1 eV [21]) are not detected. Signals will be observed from the excited species Ag_2O_2^* (VDE = 0.3 eV, s.b.) and the possible negatively charged photofragments O^- (EA = 1.462 eV [22]), Ag^- (EA = 1.303 eV [22]), O_2^- (EA = 0.44 eV [22]) and Ag_2^- (VDE = 1.06 eV [15]). All other fragment species are out of scope of our measurements.

3 Results and discussion

Figure 1 displays the ground state photoelectron spectra of Ag_2O_2^- and Ag_2^- recorded using a standard Nd:YAG laser with a photon energy of 4.66 eV. For Ag_2O_2^- , the threshold for electron emission is at a binding energy of about 2.2 eV, and the VDE is about 2.7 eV, corresponding to the maximum of the electronic transition at the lowest binding energy. The spectrum exhibits a pronounced vibrational fine structure assigned to the O–O stretching vibration (170 meV). The VDE of Ag_2^- is

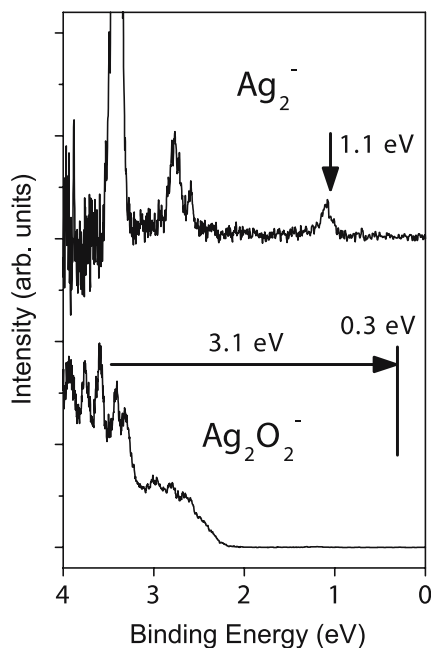


FIGURE 1 Photoelectron spectra of Ag_2^- and Ag_2O_2^- recorded using a standard Nd:YAG laser with a photon energy of 4.66 eV. The energy resolution is roughly 50 meV and varies with the binding energy. The temperature of the anions prior to detachment is about room temperature. The pronounced vibrational structure in the spectrum of Ag_2O_2^- indicates molecular chemisorption of oxygen

much lower than that of Ag_2O_2^- (vertical arrow) [15].

Figure 2 demonstrates time-resolved photoelectron spectra of Ag_2O_2^- recorded using the femtosecond laser system. The photoelectron intensity is plotted versus the kinetic energy, since two different photon energies are used and various two-photon processes might contribute to the signal. The lower trace shows a spectrum recorded exclusively with a 3.1 eV laser pulse. In this spectrum, two different features can be observed: a weak peak at a kinetic energy of 2.8 eV (marked A in Fig. 2) and an intense maximum centered around a kinetic energy of about 0.35 eV (marked C). Feature C can be assigned to direct photoemission from Ag_2O_2^- and corresponds to the maximum visible in Fig. 1 (lower trace) between 2.4 eV and 3.1 eV in binding energy. The peak at a kinetic energy of 2.8 eV (marked A) should be caused by a two-photon process. A simple two-photon process corresponding to direct photoemission should result in a peak at a kinetic energy of 0.35 eV + 3.1 eV = 3.45 eV, which is significantly higher than that of peak A. Thus, feature A must be due to two-photon excita-

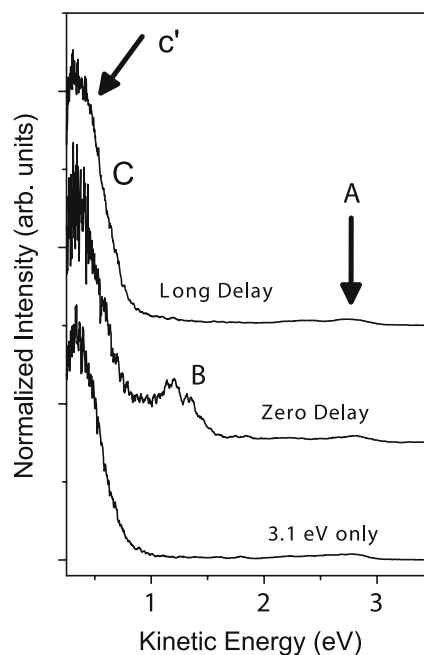


FIGURE 2 Photoelectron spectra of Ag_2O_2^- using a single femtosecond pulse with a photon energy of 3.1 eV (lower trace), two femtosecond pulses with 3.1 eV and 1.55 eV photon energies at zero delay (middle trace) and at 7300 fs delay (upper trace). Marked features are discussed in the text. No electron signal is observed with the 1.55 eV laser pulse only

tion of electrons with higher binding energies than those giving rise to the appearance of C. The standard spectrum of Ag₂O₂⁻ (Fig. 1) shows a second, more intense peak at higher binding energy range (3.4–4 eV). Applying Koopman's theorem, excitation with a photon of 3.1 eV from this state would result in a bound state with low binding energy (0.3 eV, see horizontal arrow in lower trace of Fig. 1). A second photon from the 3.1 eV pulse detaches this electron with a kinetic energy (E_{kin}) of $3.1 \text{ eV} - 0.3 \text{ eV} = 2.8 \text{ eV}$. An excess energy E_{vib} remains in the neutral Ag₂O₂, which can be estimated to

$$E_{\text{vib}} = 2h\nu - EA(\text{Ag}_2\text{O}_2^-) - E_{\text{kin}}.$$

The EA of Ag₂O₂⁻ is unknown, but the threshold energy in the photoelectron spectrum of Ag₂O₂⁻ (Fig. 1, lower trace) gives an upper limit of the EA:

$$EA(\text{Ag}_2\text{O}_2^-) < 2.2 \text{ eV}.$$

Thus, the excess energy E_{vib} in the remaining neutral Ag₂O₂ is at least

$$E_{\text{vib}} > 2 \times 3.1 \text{ eV} - 2.2 \text{ eV} - 2.8 \text{ eV} \\ = 1.2 \text{ eV}.$$

The appearance of feature A indicates the existence of an excited state of Ag₂O₂⁻ with an electron binding energy of roughly 0.3 eV, which is optically accessible by photons of 3.1 eV. Please note that the spectrum (lower trace of Fig. 2) is generated using the pump pulse only and is superimposed to all spectra obtained using both femtosecond laser pulses.

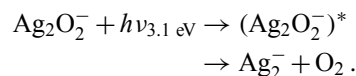
If Ag₂O₂⁻ is irradiated using both femtosecond pulses with photon energies of 3.1 eV and 1.55 eV, respectively, a new feature at a kinetic energy of about 1.25 eV appears (Fig. 2: middle trace, marked B). This feature can be explained by assuming the existence of an excited state of Ag₂O₂⁻ with an electron affinity of about 0.3 eV ($1.25 \text{ eV} = 1.55 \text{ eV} - 0.3 \text{ eV}$). The state is populated by the pump pulse (3.1 eV) and the large intensity of this two-photon feature is indicative of a large cross section for this excitation.

With increasing pump-probe delay, feature B disappears and a photoelectron spectrum resembling the one obtained using only the pump pulse is observed (Fig. 2: upper trace) with a weak

shoulder appearing on the high kinetic energy side of feature C (marked c').

The changes in the pump-probe spectra as a function of delay time become more pronounced in the difference spectra, in which the delay-independent electron signal (Fig. 2 lower trace) is subtracted (Fig. 3). Assuming an exponential decay of the optically excited state, one sees that feature B, assigned to the detachment from the excited state of Ag₂O₂⁻, disappears with a lifetime of $130 \text{ fs} \pm 70 \text{ fs}$, which is close to the time resolution of our experimental setup. In the difference spectra shoulder c' observed in Fig. 2 (upper trace) appears as a peak at a kinetic energy of 0.5 eV. Peak B decreases in intensity with increasing time interval between the pulses, whereas peak c' grows concomitantly. Since the probe photon energy is 1.55 eV, the binding energy of these electrons corresponds to $1.55 - 0.5 = 1.05 \text{ eV}$. Within the experimental error of $\pm 0.1 \text{ eV}$ this coincides with the VDE of Ag₂O₂⁻. Hence, peak c' in Fig. 3 is tentatively assigned to photofragmenta-

tion, yielding pure Ag₂⁻:

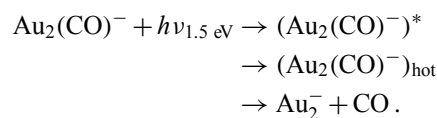


For the assignment of peak c' to this photofragmentation process, the following uncertainties should be taken into account:

(i) Identification of Ag₂⁻ as photofragment is based on the peak position of feature c', which became clearly visible only after some treatment of the raw data in the difference spectra. Shape and exact position of the peak change within certain error bars depending on the subtraction parameters.

(ii) Multiphoton processes contributing to the signal cannot be excluded. Other reaction pathways involving different neutral or charged photofragments and two or even three photons might yield a similar peak in the photoelectron spectrum. Although we kept the power of each laser pulse as low as possible, such processes cannot be completely ruled out.

Although these uncertainties should be taken into account, the process of photodesorption of neutral O₂ seems to be reasonable and similar to the known photodesorption process of CO from Au₂⁻ [10]. The latter is a thermally activated process, in which the energy of the pump photon is first thermalized and then CO desorbs from the hot anion:



In contrast to Au₂(CO)⁻, our data on Ag₂(O₂)⁻ are more suggestive of a direct photodesorption process due to the following reason:

In case of thermally activated processes each photoelectron spectrum of the TR-PES series corresponds to the superposition of parent and fragment spectra. With increasing delay, the parent spectrum decreases and the fragment spectrum increases in intensity. In case of a direct process, the time-dependent change of the electronic structure is reflected in gradually changing shapes and positions of the photoemission features. Figure 4 displays the time development of feature c' exclusively (the contribution of excited state B to the spectrum has been subtracted). A change in the

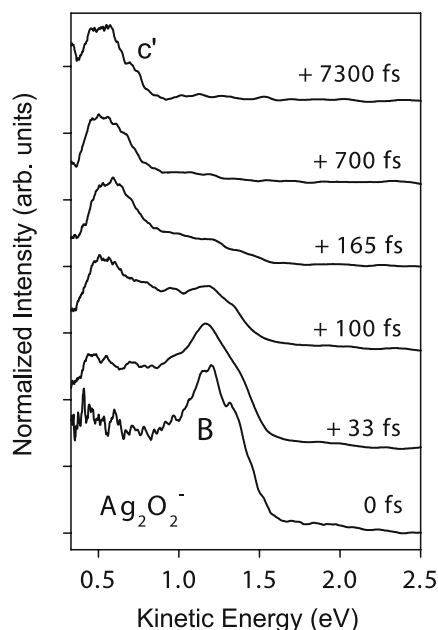


FIGURE 3 Delay-dependent part of the time-resolved photoelectron spectra of Ag₂O₂⁻. Pump and probe photon energies are 3.1 eV and 1.55 eV, respectively, with the 3.1 eV pulse being first. The pump-probe delay is given in femtoseconds. The delay-independent photoelectron signal (lower trace in Fig. 2) has been subtracted in each spectrum. The marked features correspond to the ones in Fig. 2. Feature B is assigned to an excited state of Ag₂O₂⁻ and peak c' is tentatively assigned to the peak at 1.1 eV binding energy in the spectrum of Ag₂O₂⁻ (Fig. 1: upper trace)

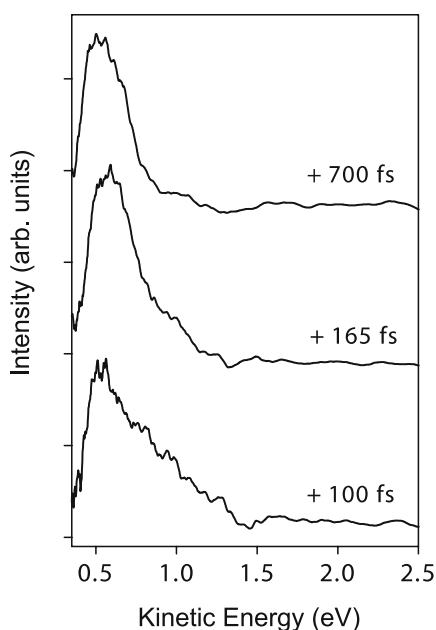


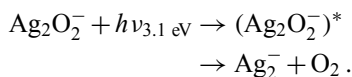
FIGURE 4 Time evolution of the shape of feature c' as extracted from the data displayed in Fig. 3. Feature B observed in the lowest trace of Fig. 3 is subtracted from each spectrum displayed in Fig. 3. The residual signal is dominated by feature c' . The procedure reveals a delay-dependent change in the shape of feature c'

shape of feature c' is visible with increasing delay time, whereas only the increase of the peak intensity without a change of peak shape is expected for a thermally activated process.

The direct process occurs within a time scale comparable to our instrumental time resolution and we are almost not able to see details in the changing of the electronic structure taking place along the O_2 desorption. The primary goal of observing the breaking of the chemical bond and the subsequent reorganization of the electronic structure is not yet reached. Summarizing our main results demonstrated so far:

(i) Unambiguously we identify an optically accessible excited state of $Ag_2O_2^-$. The optically allowed transition has a large cross section which can be qualitatively deduced from the unusual high intensity of pump-probe feature B (Fig. 2).

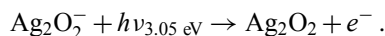
(ii) The excited state decays most likely by direct photofragmentation via the process



This is in contrast to bulk surfaces where direct photofragmentation com-

petes with efficient thermalization. Accordingly, the use of clusters instead of bulk surfaces might enhance the efficiency of photochemistry drastically.

In the next section, our results will be compared to the NeNePo studies of Socaciu–Siebert et al. on the same cluster anion [1]. The NeNePo data were suggested to be based on a one-photon pump process:



The neutral Ag_2O_2 is unbound and the O_2 molecule leaves the Ag_2 in a unimolecular decay process:



The neutral Ag_2 might be vibrationally excited (indicated by the star). The probe laser pulse then ionizes the neutral Ag_2^* in a multiphoton process. The intensity of Ag_2^+ is recorded with respect to the pump-probe delay. The ion signal varies periodically as a function of time delay between pump and probe pulse and the frequency is assigned to the Ag_2^* stretching vibration. This vibrational frequency is red shifted compared to the one of the NeNePo signal of bare Ag_2^- . The authors interpret this behaviour as a vibrational excitation with an excess energy of 0.7 eV in the neutral Ag_2 after desorption of an O_2 molecule.

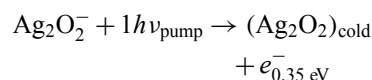
The NeNePo data agree with our TR-PES spectra, assuming that the pump pulse detaches the electron from $Ag_2O_2^-$ in a two-photon process via the excited state of the anion. In the TR-PES this two-photon process gives rise to feature A in Fig. 2. The kinetic energy of the detached electron is 2.8 eV, and the electron affinity of $Ag_2O_2^-$ is below 2.2 eV (threshold of the lower trace in Fig. 1). The energy balance leaves an excess energy of 1.2 eV in the neutral Ag_2O_2 as calculated above ($1.2\text{ eV} = 2 \times 3.10\text{ eV} - 2.8\text{ eV} - 2.2\text{ eV}$). The O_2 desorption requires some energy so that an excess energy of 0.5–0.8 eV may remain in the neutral Ag_2 explaining the red shift in the NeNePo data.

Thus, based on our TR-PES data, we may reassign the first step of the NeNePo data to two-photon detachment of the pump pulse via the excited state of the $Ag_2O_2^-$ anion. This specific two-photon process leaves an excess energy

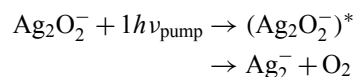
in the neutral Ag_2O_2 and this energy probably causes the O_2 desorption.

In our TR-PES experiment, we populate this excited state with a one-photon process and its decay is recorded using the probe pulse. The (unwanted) two-photon pump process leads to the appearance of an additional weak feature (A) in the photoelectron spectra. The direct photodetachment of $Ag_2O_2^-$ can be viewed as a third competing process leaving almost no excess energy in the neutral Ag_2O_2 (Fig. 2: feature C). We are not able to observe the further fate of this relatively “cold” neutral Ag_2O_2 . Summarizing, there are three processes corresponding to the three features A, B and C in Fig. 2:

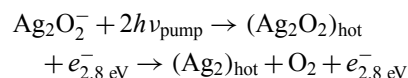
Process I: Feature C: One-photon detachment



Process II: Feature B: One-photon excitation of the anion and subsequent desorption



Process III: Feature A: Two-photon detachment



With TR-PES we studied process II, while in the previous NeNePo experiment most likely process III was detected. The observation of hot neutral Ag_2 is a consequence of the existence of the excited state of $Ag_2O_2^-$. A one-photon pump-process in case of the NeNePo experiment can be excluded, because there is not enough energy left in the neutral to explain the red shift of the vibrational frequency. The electron from single photon detachment has a kinetic energy of about 0.35 eV (feature C in Fig. 2) and the residual energy for Ag_2O_2 is negligibly small.

4 Conclusion

We studied the photodesorption of Ag₂O₂⁻ using TR-PES. The excitation by a pump pulse with a photon energy of 3.1 eV leads to the formation of an excited state of the anion. Most likely, the state decays in a direct photodesorption process with a lifetime of 130 fs ± 70 fs into O₂ and Ag₂⁻. Our data indicate the existence of two other processes: the regular one-photon detachment leading to the electronic ground state of the neutral Ag₂O₂ and a resonant two-photon detachment process via the excited state leading to hot neutral Ag₂O₂. In the latter case the excess energy is a consequence of the anion's excited state configuration which does not allow a transition into the electronic ground state of neutral Ag₂O₂. Most likely, the latter process is the one observed in the NeNePo experiment of Socaciu–Siebert et al. [1]. This resonant two-photon detachment might dominate at slightly higher pump pulse energies. Our primary goal to directly observe the reorganization of the electronic structure during the direct photodesorption is not yet reached, because the process is too fast to be completely resolved with

our instrumental time resolution. The analogous process for larger silver clusters such as Ag₃O₂⁻, Ag₄O₂⁻ and Ag₈O₂⁻ is subject of future studies.

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