

Relaxation dynamics of the Au_3^- and Au_6^- cluster anions

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Abstract

Using TR-2PPE spectroscopy, direct evidence is provided that excited states of sp-metal clusters can live longer than one nanosecond. For Au_3^- , in addition, the high time resolution in the present work allows us to monitor the wave-packet motion in the real time scale. The relaxation times of the Au clusters are estimated to be longer than those of the Al clusters with similar sizes by about three orders of magnitude. This result is attributed to the larger gaps between various energy levels in Au clusters originating from relativistic effects, which markedly reduce the e-e scattering rates.

Developments of the Time-Resolved Two Photon Photoemission (TR-2PPE) Spectroscopy using femtosecond laser opened insights into the dynamics of the chemical reactions and optically excited states in molecules and solids [1–14]. Recently, the application of this technique has been extended to mass-selected nanoclusters [15–19]. It has been shown that the lifetimes of the optically excited states in small d-metal clusters consisting of less than seven atoms are comparable to those of the respective bulk crystals [15–18]. This result was attributed to the fact that in the small d-metal clusters the numbers of the unoccupied electronic levels within the excitation energies are large enough to ensure the fast Auger-like electron–electron scattering [16]. In contrast to the d-metal clusters, the

experimental results of the sp-metal clusters show much longer lifetimes (several hundreds of picoseconds or even longer) for the excited states, which originate from the lower density of states in the sp-metal clusters [20–22]. For example, Ag_8 in an Ar matrix exhibits fluorescence phenomena, indicating that the decay of the optically excited states in Ag_8 should take place on a nanosecond (ns) time scale [20]. Wave-packet motions along the internuclear distance were observed for Na-dimers, also implying the existence of the very long-living excited states [21]. The fragmentation of Au_3^- into Au_2 and Au by optical excitations is an evidence for a long decay time of Au_3^- [22]. Yet, the relaxation dynamics of the sp-metal clusters have been rarely monitored using TR-2PPE spectroscopy with a sufficiently high time resolution.

It is important to mention that the relaxation dynamics of optically excited states can be understood considering the competition between

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transition and screening; on one hand, considering the screening effect, the relaxation rate should be reduced, when the density of states (DOS) becomes lower. On the other hand, the lowered DOS decreases the inelastic electron–electron scattering rate, thus reducing the relaxation time. That the sp-metal clusters consisting of less than 10 atoms show much longer lifetimes of the optically excited states than those of the d-metal clusters suggests that for the nanoclusters consisting of less than 10 atoms, the relaxation rate is governed by the e–e scattering, whereas the screening effect plays a minor role.

To shed light on the relaxation dynamics of sp-metal clusters, TR-2PPE spectroscopy experiments were recently performed for Al_n^- for $n = 6\text{--}15$ in our group [24]. In contrast to the common expectation that the excited states in these clusters should live much longer than those of d-metal clusters, the decay times of these Al clusters have been found to be of the orders of several hundreds of femtoseconds (fs), which is comparable to the values determined for the d-metal clusters [24]. In particular, Al_{13}^- , which is a magic cluster with a large gap between the Highest Occupied Molecular Orbital and the Lowest Unoccupied Molecular Orbital (HOMO–LUMO gap) [25,26], shows faster relaxation dynamics than those of other non-magic clusters. This cannot be explained by the Auger-like electron–electron scattering within the frozen orbital scheme. Further studies are essential to better understand the origin of the fast relaxation dynamics of the magic cluster Al_{13}^- . This result invokes a question: Are there any other examples for the extremely fast relaxation dynamics for the magic clusters, or is Al_{13}^- an exception? An answer to this question can be provided by accumulating ample experimental data on relaxation dynamics of various metal clusters with large gaps between different electrons levels.

This work aims at obtaining a better insight into the relaxation dynamics of Au anion clusters. Direct evidence is provided that the relaxation dynamics of the sp-metal clusters can take place on the nanosecond time scale. For Au_3^- , a lifetime of about 1.2 ns was found, in agreements with previous studies [22]. Higher time resolution in the

present work allows us to monitor the wave-packet motion along the internuclear distance in the real time scale, which was hardly resolved in the previous work. In contrast to the results from Al_n^- with $n = 6\text{--}15$ Au_6^- clusters show relaxation times between several hundreds of picoseconds and several nanoseconds, which can be explained by a large gap between the HOMO and the next electronic levels in Au_6^- [27].

Au anion clusters are produced by means of a pulsed arc cluster ion source and mass-selected using a time-of-flight mass spectrometer. A selected bunch of cluster anions is irradiated by two pulses generated in a femtosecond laser system [19,24]. The cluster temperature is estimated to be room temperature, and the energy resolution of our photoemission spectra is about 0.1 eV. The first pulse (pump pulse) has a photon energy of 1.5 eV (red pulse) and the second pulse (probe pulse) a photon energy of 3.05 eV (blue pulse) with a width of about 60 fs for each pulse. The pump pulse results in photoexcitation of a certain fraction of the anions in the bunch and the probe pulse detaches electrons from a fraction of the anions in the same bunch. The photon flux of both pulses has to be optimized to maximize the number of species hit by a single photon of each pulse, and to minimize the number of species hit by two or more photons from one of the pulses. For the pump pulse alone, this has been achieved by adjusting the photon flux gain to less than 10% with respect to photoelectron intensity created by two-photon process of the pump pulse. This procedure minimizes the ‘false’ two-photon pump electron signal with respect to the ‘true’ pump–probe signal. The same procedure has been applied to the adjustment of the photon flux of the probe pulse minimizing two-photon processes of the probe pulse alone, which can be easily detected by the appearance of electrons at higher kinetic energies. The photon flux of both pump and probe pulses have to be readjusted for different clusters, because the cross sections of the corresponding processes may vary significantly as a function of cluster size.

We have studied relaxation dynamics of Au_n^- with $n = 1\text{--}6$. Except for Au_3^- and Au_6^- , the experiments for other Au anion clusters yielded extremely short lifetimes of the excited states, which

are quite close to the experimental resolution of our femtosecond laser system. These results are attributed to the non-resonance two-photon process, implying that the fixed photon energies in our laser system do not allow excitations into the resonance states of these clusters. These results indicate a very low density of state in these clusters, i.e., the distances between different energy levels are quite large. In fact, Au clusters exhibit much larger splittings of Molecular Orbitals (MO) compared to other metal clusters, since the Au–Au bonding is much stronger than those of other metals due to the relativistic effects [20]. As a result of the larger MO splitting, Au clusters show a much larger even/odd alteration of the electron affinity as a function of cluster size with respect to other metal clusters (Fig. 1). In contrast to the result of the present work, experiments on Al anion clusters with $Al = 6-15$ always ended up with

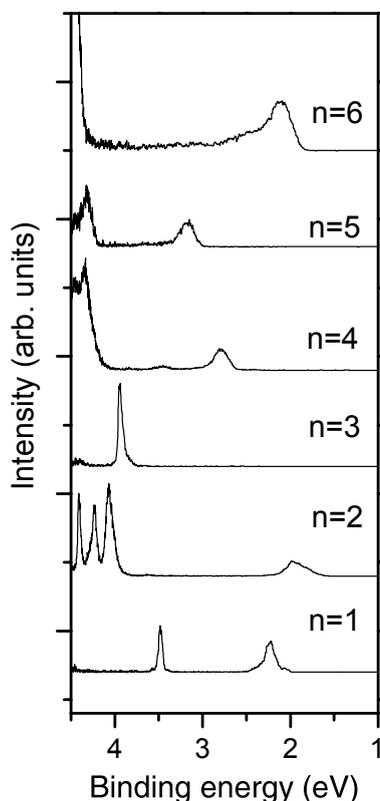


Fig. 1. UPS spectra of the Au anion clusters ($n = 1-6$) with a photon energy of 4.66 eV.

lifetimes of the excited states which can be attributed to the resonance states. This result can be rationalized by much higher densities of states in the Al clusters [24].

We concentrate on results of Au_3^- and Au_6^- , for which excitations to the resonance states were allowed in our laser system. In Fig. 2, an overview of a TR-2PPE spectrum for Au_3^- in a wide energy range with a time delay of 50 picoseconds is displayed. The features at 2.7 eV are attributed to the signals from one-photon excitations by the pump pulse and two-photon detachment by the probe pulses. Other features at lower binding energies are caused by two-photon processes of the pump pulse, which do not depend on the pump-probe delay.

In Fig. 3, the pump + two probe features centered at about 2.6 eV are shown for various time intervals between pump and probe pulses. In agreement with the previous results from our group, the lifetime of the excited state in Au_3^- was estimated to be about 1.2 ns [22]. We have used a photon energy of 1.5 eV for the pump pulse, whereas 3.05 eV was utilized in [22]. Though, we came up to a very similar spectrum to that in [22], most likely due to the two photon detachment process in the present work caused by sufficiently high infrared beam intensities. The lifetime was determined assuming an exponential decay of the pump/probe signal as a function of time interval

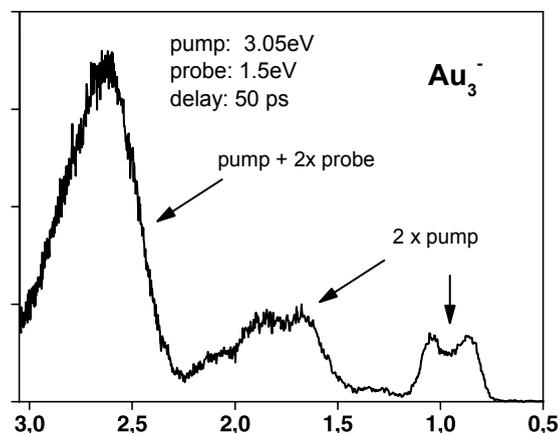


Fig. 2. TR-2PPE spectrum of Au_3^- with a binding energy range between 0 and 3 eV.

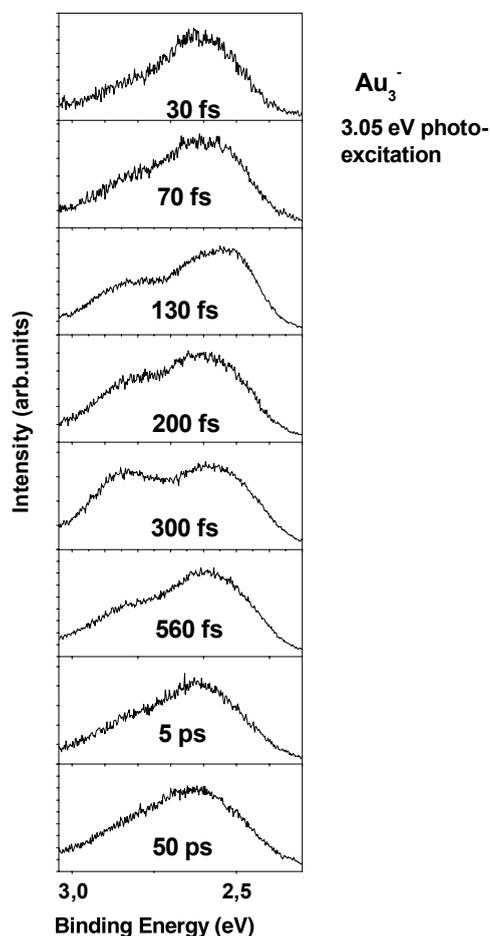


Fig. 3. TR-2PPE spectra of Au_3^- with various time intervals between pump and probe pulses. Only the signals originating from one pump pulse and two probe pulses are displayed.

between the pump and probe pulses. In addition, the much higher time resolution in the present work allowed us to detect the fine structures at about 2.5–3.0 eV, which was not clearly resolved in the previous work. With increasing time intervals between pump and probe pulses, a peak appears at about 2.5 eV (see 130 fs in Fig. 1). For 200–300 fs, an additional feature at 2.8 eV can be detected, whereas the peak 2.5 eV is concomitantly reduced. For time intervals longer than 5 picoseconds (ps), the doublet feature develops into a broader single peak centered at about 2.6 eV.

The most probable explanation for the appearance of the fine structures is that the fast vi-

brational wave-packet is monitored in real time. As a consequence of the Franck–Condon principle, the geometrical structure of the excited state should initially be much different from the equilibrium structure of the excited state. The peak at 2.5 eV, visible for the time interval of 130 fs is likely to correspond to the electronic state of a cluster geometry far away from the equilibrium structure. Within several hundreds of femtoseconds, however, the Au atoms move towards the equilibrium position. Due to the excess energies in the cluster at this stage, the atomic positions pass over the equilibrium position and move away from the equilibrium position, yielding the peak at 2.8 eV for the time interval between 130 and 560 fs (Fig. 3). Then, the structure is driven back to the equilibrium position. Within this oscillation of the atomic positions around the equilibrium structure of the excited state, excess energies are slowly dissipated into the degrees of freedom of the Au_3^- . When the excess energy in the cluster driving this oscillation is completely converted into the degrees of freedom of the cluster, a broader feature replaces the doublet feature. An analogous vibrational wave-packet motion has been monitored in previous femtosecond TR-2PPE Spectroscopy experiments for the Na-dimers by Baumert et al. [21]. By comparing our results to those of the Na-dimer, the motion of the wave-packet for Au_3^- is much slower than that of Na-dimer. Previous studies on Ag_3 clusters have shown that the linear and triangular structures Ag_3^- are the minima in the potential energy surface. For anionic clusters, the ground state has the linear structure, whereas for the excited states and neutral clusters, the triangular structure is energetically more stable than the linear one [28,29]. One may assume that the potential energy surface of Au_3 is analogous to those of Ag_3 . The linear Au_3^- clusters can try to form a triangular structure upon excitation by a pump pulse, and the wave-packet motion in Au_3^- observed in Fig. 3 most likely corresponds to the oscillation between the linear and the triangular structure of Au_3^- (bending mode). The broadening of the spectra for 50 ps delay with respect to the time intervals less than 100 fs is consistent with the energy dissipation into the nuclear degrees of freedom.

The vibrational wave-packet motion can be only monitored in real time, when the lifetime of the excited state is long enough to ensure the vibrational wave-packet motions to occur, before the excited state decays through the electron–electron scattering process. It is likely that the observation of the wave-packet motion in TR-2PPE spectroscopy should be relevant for other small *sp*-metal clusters.

For Au_6^- , two different sets of TR-2PPE spectra are illustrated in Fig. 4. The first set of the spectra corresponds to the blue/red excitation, i.e., Au_6^- clusters are first excited by the 3.05 eV photon, and then probed using the 1.5 eV. The second data set is taken using a pump pulse with a photon energy of 1.5 eV and the 3.05 eV probe pulse. In both

cases, a narrow single peak appears at the binding energy of 0.8 eV. This peak is still present for the time interval of several hundreds of picoseconds between the pump and probe pulses. Assuming an exponential decay of the optically excited states in Au_6^- , we estimate the lifetimes of the two different excited states observed in the blue/red and red/blue experiments to be 1.2 ns and 0.5 ns, respectively.

The lifetimes of the excited states in Au_6^- are markedly longer than that of Al_6^- , which is about 500 fs [23]. Different optical properties of Au_6^- and Al_6^- can be explained by the unusual electronic structures of Au clusters with respect to other clusters. The interatomic interaction between Au is much stronger than in the case of other metals due to relativistic effects [27], which increase the bond

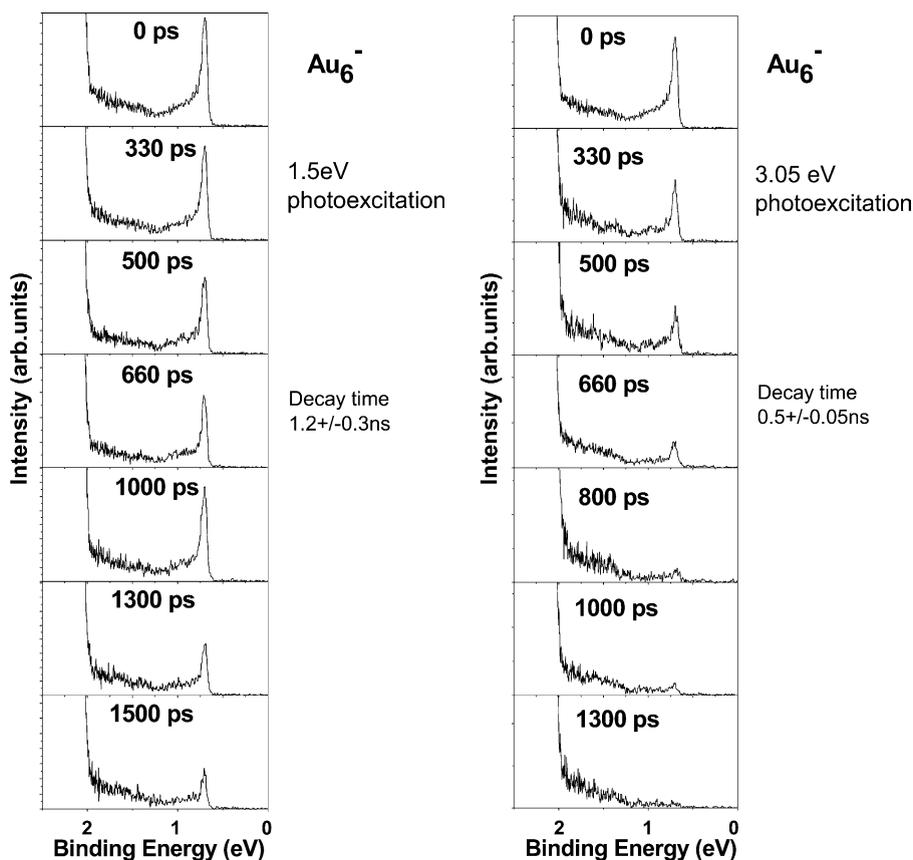


Fig. 4. TR-2PPE spectra of Au_6^- with various time intervals between pump and probe pulses. The data set on the left side corresponds to the blue/red experiments (pump: 3.05 eV, probe: 1.5 eV), whereas those on right results from the red/blue experiments (pump 1.5 eV, probe 3.05 eV).

enthalpy and enlarge the splitting of the MOs produced by linear combinations of the valence s orbitals. A larger gap between different valence electronic levels caused by the larger MO-splitting can then reduce the Auger-like electron–electron scattering rate, which results in the much larger lifetimes of the excited states in Au_6^- .

This is the first direct measurement of a lifetime of an excited state in a metal cluster (i.e., a cluster consisting of metal atoms) larger than a trimer in the nanosecond time regime. Such a long lifetime is rather unexpected for 'metallic' nanoparticles and indicates semiconducting properties of the clusters.

In conclusion, using femtosecond TR-2PPE spectroscopy, we observed extremely long-living excited states in the Au anion clusters, which decay on the nanosecond time scale. For Au_3^- , a lifetime of about 1.2 ns was determined, in agreement with previous studies [22]. The higher time resolution in the present work allows us to monitor the wavepacket motion in real time, which has been hardly resolved in the previous work. The lifetimes of the Au_6^- clusters are longer than those of Al clusters with similar sizes by three orders of magnitude. This result can be explained by a large gap between HOMO and the next electronic levels in Au_6^- , which results from the relativistic effects.

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