

Symmetry-induced long-lived excited state in Au_6^-

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We present time-resolved photoelectron spectra in combination with quantum chemical calculations based on time-dependent density functional theory for the study of the long-lived excited state of Au_6^- . The experimental spectra indicate an excited state lifetime of at least 90 ns. It is shown that the orbital symmetry of the photoexcited state as well as the planarity of Au_6^- are responsible for the unusual long lifetime. A possible decay mechanism is the fluorescence of a photon which is estimated to take place on a time scale of 730 ns.

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I. INTRODUCTION

Reducing the size of bulk metals down to small clusters consisting of only a few atoms has a significant impact on the optical properties. Due to quantum confinement, the continuous band structure of a bulk metal develops into discrete atomiclike energy levels (see, e.g., Ref. 1 and references therein). While optical excitations in bulk noble metals relax within around 1 ps into thermal equilibrium,^{2,3} in small noble metal clusters, the respective lifetimes can be significantly longer. Indirect evidence for long-lived electronically excited states in clusters first came from the observation of fluorescence in Ag clusters deposited in a noble gas matrix.⁴ Later on, Au_6^- was studied using time-resolved photoelectron spectroscopy.⁵ A decay time of the 1.5 eV excited state of 1.5 ns was determined from an exponential fit. According to our experimental results presented here, we must conclude for an even much longer lifetime of at least 90 ns for the same excited state. This result is supported by our time-dependent density functional theory (TDDFT) calculations. One explanation for such a long lifetime in metal clusters can be found in the discrete electronic density of states in the highest occupied molecular orbital and lowest unoccupied molecular orbital (HOMO-LUMO) region of these systems. Noble metal clusters consisting of only a few atoms can therefore be considered as molecular rather than bulklike systems. As a consequence, bulklike relaxation processes such as inelastic electron-electron scattering that appear on a time scale of much less than 100 fs are very unlikely. However, vibrational relaxation processes such as vibrational wave packet motion,⁶ intravibrational energy redistribution,⁷ or the cluster analog to electron-phonon scattering^{8,9} are observed on a picosecond time scale in systems where electronic relaxation processes do not dominate. Excited state lifetimes on a nanosecond time scale can only appear when none of the above mentioned relaxation processes are taking place.

The Au_6^- cluster attracted considerable attention in the past due to its extraordinary large band gap which amounts to 2.3 eV.¹⁰ Experimental techniques such as ion mobility measurements as well as photoelectron spectroscopy in com-

bination with relativistic density functional calculations revealed that Au_6^- exhibits a flat D_{3h} triangular geometry.¹¹⁻¹³ The stability of this structural configuration as well as the large gap can be understood in a model of delocalized electrons in a triangular potential.¹⁴ Six delocalized electrons close a shell in this model, leading to the observed HOMO-LUMO gap. So far, the excitation spectrum of gold cluster anions has been studied only for Au_N^- ($N \geq 7$).¹⁵ To our knowledge no absorption spectrum of Au_6^- is available in the literature.

We conducted a combined experimental and theoretical study on the time-dependent behavior of photoexcited Au_6^- . The experimental time window is extended to 90 ns which is almost two orders of magnitude larger as compared to the former measurements.⁵ A study of the experimental processes by *ab initio* calculations helps us to understand this unexpected time-dependent behavior: The symmetry of the involved states together with the planar geometry of Au_6^- lead to a metastability of the excited state.

II. METHODS

Experiment. Gold cluster anions are produced using a pulsed laser-vaporization source.¹⁶ In a supersonic expansion within helium buffer gas, the clusters are cooled well below room temperature.¹⁷ Before entering the interaction zone of a magnetic bottle photoelectron spectrometer, the cluster anions are mass selected and decelerated. Time-resolved photoelectron spectra are taken using the output of an amplified Ti:Sa femtosecond laser system (fundamental of 1.56 eV, pulse energy of <1 mJ, pulse duration of 40 fs full width at half maximum, intensity of 10^{11} W/cm²). In a pump-probe scheme absorption of the “pump” pulse leads to the population of the second electronically excited state (B^-) in Au_6^- . The ensuing dynamics is monitored by subsequent photodetachment using a second “probe” pulse. We use the fundamental (1.56 eV) as the pump and the second harmonic (3.12 eV) as the probe pulse. The time delay t between the pulses can be adjusted in the range of $-750 < t < 750$ ps by varying the optical path using a computer controlled delay stage. The time axis is calibrated by determining the point of

zero delay time between pump and probe pulse directly inside the interaction region. This is achieved by generating the third harmonic using a β -barium borate (BBO) crystal which is mounted inside the vacuum chamber. For long delay times ($20 < t < 100$ ns), we use the 1.56 eV femtosecond pulse as the pump and the third harmonic of a Nd doped yttrium aluminum garnet (Nd:YAG) laser as the probe pulse ($h\nu = 3.5$ eV). The temporal resolution for the femtosecond-pump Nd:YAG-probe setup amounts to ± 10 ns. In each case, both laser pulses enter the interaction region collinearly. We note that the intensity of the pump laser has to be carefully adjusted in order to avoid three-photon photoemission with the pump laser. In Au_6^- , for example, this could cause a time-independent background signal at the binding energy of 0.6 eV, which would overlap the time-dependent feature.

Ground-state density functional theory calculations. The atomic and electronic structures of the $\text{Au}_6/\text{Au}_6^-$ clusters were calculated within the density functional theory (DFT) in combination with Born-Oppenheimer molecular dynamics^{13,18} including self-consistent gradient corrections via the so-called Perdew-Burke-Ernzerhof generalized gradient approximation functional.¹⁹ Scalar-relativistic nonlocal norm conserving pseudopotentials devised by Troullier and Martins²⁰ were employed on the $5d^{10}6s^1$ valence electrons of gold. The Kohn-Sham states were expanded in a plane wave basis set using a kinetic energy cutoff of 62 Ry.

Linear-response time-dependent density functional theory calculations. We follow the formulation of the linear-response time-dependent DFT given by Casida,²¹ as implemented in Ref. 22. The evaluation of polarization resolved spectra is described in Ref. 23. For the sake of consistency, the exchange-correlation kernel was evaluated within a finite difference scheme²⁴ using the gradient corrected exchange-correlation potential.

III. RESULTS AND DISCUSSION

Time-resolved photoelectron spectra are shown in Fig. 1. The photoelectron yield is plotted over the binding energy (BE), which is defined as the energy difference between the photon energy and the measured photoelectron kinetic energy. The probe-only spectrum (bottom curve) was recorded by photodetachment using the 3.12 eV femtosecond laser. It shows a single peak at 2.2 eV binding energy. This peak corresponds to the vertical transition from the electronic ground state of the anion (X^-) into the electronic ground state of the neutral cluster (X), i.e., the vertical detachment energy (VDE). The measured energy is in agreement with the previously measured VDE of 2.13 eV (Ref. 13) and the calculated value of 2.29 eV.^{11,13} The pump-probe spectra have been recorded by additionally irradiating the clusters with the femtosecond-pump pulse ($h\nu_{\text{pump}} = 1.56$ eV). For negative delay times, the probe pulse precedes the pump pulse and no photoemission intensity is observed at a binding energy below the VDE. The absence of photoelectrons at negative delay times clearly indicates that no multiphoton photoemission by the pump laser takes place in contrast to the former measurements.⁵ When temporal overlap between pump and probe pulse is reached, a photoelectron peak

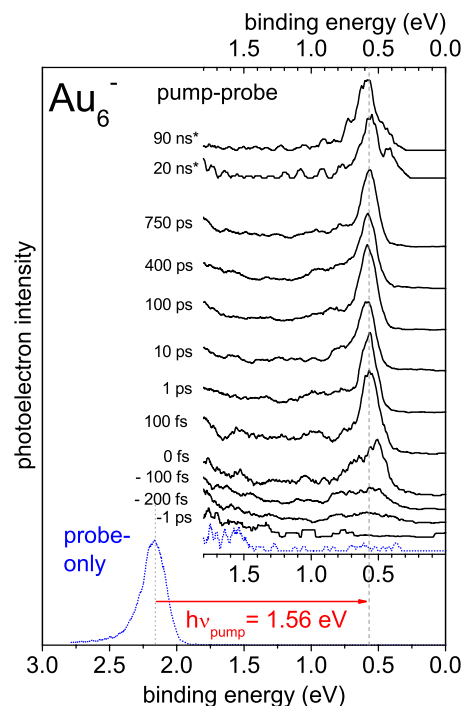


FIG. 1. (Color online) Time-resolved photoelectron spectra of Au_6^- . The dotted blue lines correspond to the probe-only spectrum ($h\nu_{\text{probe}} = 3.12$ eV). The black spectra have been recorded using two-photon photoemission with photon energies $h\nu_{\text{pump}} = 1.56$ eV and $h\nu_{\text{probe}} = 3.12$ eV. (*) The 20 and 90 ns spectra have been recorded using a Nd:YAG-probe laser (for details, see text).

evolves at 0.6 eV binding energy. As will be revealed by the TDDFT calculations, this peak is due to the population of the second electronically excited state of the anion (B^-) and subsequent photodetachment using the probe pulse. The binding energy of this two-photon photoemission peak $\text{BE} = \text{VDE} - h\nu_{\text{pump}}$ shows that after photodetachment, the electronic ground state of the neutral cluster X is reached. With increasing delay time, the peak does not exhibit any change neither in intensity nor in shape or binding energy in the measured time window of 90 ns. The storage time of the clusters in the interaction region amounts to about 100 ns. Therefore, we experimentally deduce an excited state lifetime of the B^- state of at least 90 ns. We note that the decay time observed here exceeds the value given in Ref. 5 by almost two orders of magnitude. In spite of the apparent decay observed in Ref. 5, we believe in our measured extraordinary long lifetime because the intensity does not decay, neither between 0 and 1 ns nor between 20 and 90 ns. Furthermore, due to a careful normalization of the measured spectra to the one-photon photoelectron peak intensity, a proper adjustment of the pump-laser intensity in order to avoid three-photon processes at negative delays, a stable laser-vaporization cluster source, and a well defined zero-time measured inside the vacuum chamber, we are convinced of our data.

To get more insight into the underlying processes leading to the experimentally observed photoelectron spectra, we have calculated the absorption spectrum of Au_6^- , as shown in

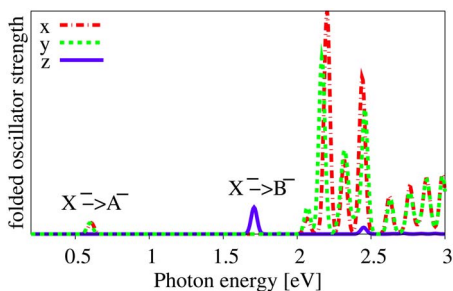


FIG. 2. (Color online) The polarization resolved TDDFT absorption spectrum of the ground-state isomer of Au_6^- . The coordinates are defined, as shown in Fig. 3. The contributions of the different polarization directions are indicated by the dashed (red), dotted (green), and solid (blue) lines. The predicted transition $X^- \rightarrow A^-$ is not probed in this experiment but only the transition $X^- \rightarrow B^-$.

Fig. 2. The planar ground-state isomer of Au_6^- was used in the calculation (configuration II in Fig. 3). The spectrum is very sparse below 2 eV photon energy, showing merely two excited states, i.e., the state A^- at 0.6 eV and B^- at 1.71 eV. The only excited state which can be populated in the time-resolved photoelectron spectroscopy scheme by using an excitation energy of $h\nu_{\text{pump}} = 1.56$ eV is the B^- state. The energy difference between experiment and theory is within the known accuracy of TDDFT.^{21,22} More insight into the nature of the transitions can be gained by using their polarization dependence.²³ Here and in the following, we use the coordinate system, as shown in Fig. 3, where the z axis is perpendicular to the cluster plane. As shown by the spectrum in Fig. 2, the B^- state can only be excited by z polarized light, i.e., light polarized perpendicular to the cluster plane. This is quite unusual for gold clusters; as usually, the lowest energy excitations are for light polarized along the largest cluster axis.²³ The latter behavior is clearly seen both in the excitation to the A^- state as well as in the next excitations above 2 eV.

Decomposing the X^- to B^- transition in the Kohn-Sham (KS) picture shows that it consists of 99.8% of a transition from the highest occupied molecular orbital (HOMO) into an empty KS state of delocalized character and p_z symmetry. The corresponding orbitals are shown in Fig. 4. This transition results in a depletion of electron density from the cluster

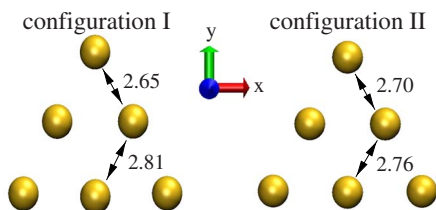


FIG. 3. (Color online) The relaxed ground-state configurations of Au_6 (configuration I) and Au_6^- (configuration II). The independent bond lengths are given in Å.

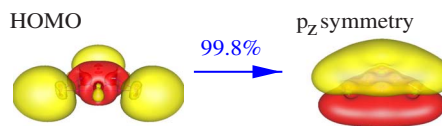


FIG. 4. (Color online) Kohn-Sham orbitals mainly contributing to the transition from X^- to B^- .

plane leaving the gold atoms effectively in the force field of a neutral Au_6 cluster. Therefore, the atoms can be expected to relax to the ground-state configuration of neutral Au_6 after excitation to the B^- state. This behavior based on the single particle picture is confirmed by comparing the state energies for the relaxed structures of the neutral (structure I) and the anionic Au_6 (structure II), given in Table I. The structures are presented in Fig. 3. Both show D_{3h} symmetry. The interatomic distance of the inner triangle atoms amounts to 2.81 Å (neutral) and 2.76 Å (anion). The bond length of the outer triangle atoms amounts to 2.65 Å (neutral) and 2.70 Å (anion). The contraction of the inner triangle and the elongation of the outer bonds can be easily understood by the structure of the HOMO of the anion (see Fig. 4), which has bonding character in the central region and antibonding nodes in the outer region.

In Table I, we compare the energies of the electronic ground and excited states as calculated for the fixed structures I and II. The electronic ground state of the neutral (X) is 0.06 eV lower in energy in structure I than in structure II, while for the electronic ground state of the anion (X^-), structure II is energetically more favorable by 0.04 eV. In the case of the B^- state structure I, i.e., the neutral ground-state structure, is energetically more favorable than structure II by 0.08 eV. Hence, this excited state shows exactly the expected behavior of preferring the structure with one electron less in the cluster plane.

The experimentally observed BE of the emitted photoelectron is given by the energy difference between X and B^- . As shown in Table I, this energy is almost independent of the structure. Therefore, the nuclear motion in the cluster plane has no impact on the energy of the emitted electrons. This gives an explanation for the persistent binding energy of the time-dependent peak, as observed in Fig. 1. The preference of structure I over structure II in the B^- state shows, however, that nuclear motion in the cluster plane is expected to be induced by this excitation.

The special p_z symmetry of the B^- state has further consequences: The nuclear motion in the cluster plane does not

TABLE I. State energies in eV for the configurations, as shown in Fig. 3. The energies are given as formation energies, i.e., the energy difference to the separated Au atoms.

	Configuration I	Configuration II	$\Delta(\text{I-II})$
E_{X^-}	13.37	13.41	-0.04
E_X	11.18	11.12	0.06
E_{B^-}	11.78	11.70	0.08
$\text{BE} = E_{B^-} - E_X$	0.60	0.58	0.02

lead to a coupling of the B^- state with neither the X^- ground state nor the A^- state. This could only take place if a strong distortion out of the planar geometry could be induced, which is not the case here. Therefore, the B^- state represents a metastable excited state which can only decay by spontaneous emission of a z -polarized photon. The corresponding decay time can be estimated by calculating the Einstein A coefficient according to²⁵

$$A = \frac{e^2}{2\pi\epsilon_0 c^3 m_0} \omega^2 f, \quad (1)$$

where ω is the transition frequency times 2π , f the dimensionless absorption oscillator strength, e the elementary charge, ϵ_0 the vacuum permittivity, c the speed of light, and m_0 the electron mass. Using the experimental energy and the TDDFT oscillator strength ($f=0.013$) corresponding to the transition from X^- to B^- , we obtain a decay time of $\tau=1/A=730$ ns. This is far above the experimental time window in which the clusters stay in the interaction region.

An alternative decay mechanism is given by nonadiabatic coupling of the B^- state to either the X^- or the A^- excited state via the out of plane vibrations. The calculation of the transition probabilities requires the evaluation of nonadiabatic matrix elements,²⁶ which is out of scope of our static TDDFT approach. The experiment does not show signs of these processes; hence, these effects must be weak. This can be understood since the out of plane vibrations are soft (around 30 cm^{-1} in our calculation) and lead to low nuclear velocities perpendicular to the cluster plane. Again, the special p_z symmetry of the B^- state requires the leading term of the nonadiabatic coupling²⁶ to be proportional to the nuclear velocity in z direction and the low velocity might be the obstacle for this decay channel.

We performed a similar analysis for other planar gold ground-state isomers of Au_n^- , where $n=5,7-10$.¹³ In these

systems, we do not observe an energetically well isolated p_z state. This is in agreement with our recent experimental study of Au_n^- ($n=5,7,8$) (Ref 27), where such an extraordinary long lifetime is not observed.

IV. CONCLUSION

We have used time-resolved photoelectron spectroscopy with an increased time window to study the 1.56 eV excited state of Au_6^- . According to these measurements, the lower limit for the excited state lifetime has been determined to 90 ns, which exceeds the literature value by two orders of magnitude. This unusual behavior is explained by the planar geometry of Au_6^- and the special symmetry of the photoexcited state. We have presented the TDDFT absorption spectrum of Au_6^- . It was shown that the measured photoelectron binding energy is independent of geometry changes in the cluster plane which explains that no binding energy changes are observed experimentally. Geometry distortions of the out of plane, which could enable nonradiative decay mechanisms out of the B^- state, are not taking place. The proposed decay channel is spontaneous emission of a z -polarized photon. The estimated decay time amounts to 730 ns which is far above the experimental time window.

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