



Elucidating the Doping Effect on the Electronic Structure of Thiolate-Protected Silver Superatoms by Photoelectron Spectroscopy

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Terminology

- Vertical detachment energy (VDE): It is the most probable and intense transition corresponding to the vibrational excited state of the positive ion that has the same geometry as the neutral molecule.
- ❑ Adiabatic electron affinity(AEA): It is given by the difference between the energy of the neutral system at its most stable geometry, and of the anionic cluster, also at its most stable conformation.
- Repulsive Coulomb barrier (RCB): It is the energy barrier experienced by an electron which is emitted from a multiple charged anion. the electron experiences shortrange attraction by the nuclei and long-range repulsion from the remaining negatively charged system, giving rise to the RCB.
- □ Thermionic emission (TE): A slow emission of electrons from a heated source, suppressing direct electron detachment and dissociation into anionic fragments.

Background Work



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Background Work

Article

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Photoinduced Thermionic Emission from $[M_{25}(SR)_{18}]^-$ (M = Au, Ag) Revealed by Anion Photoelectron Spectroscopy

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Article

Understanding Doping Effects on Electronic Structures of Gold Superatoms: A Case Study of Diphosphine-Protected $M@Au_{12}$ (M = Au, Pt, Ir)

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Electrochemical analysis demonstrated that the energy levels of the HOMO are upshifted in the order of Au₁₃ < PtAu₁₂ < IrAu₁₂, which is explained as, the jellium core potential at the central position becomes shallower by replacing Au⁺ with Pt⁰ and further with Ir⁻. A gradual increase of the energy gap between HOMO and LUMO in the order of Au₁₃ < PtAu₁₂ < IrAu₁₂ was observed here.

Motivation

- Doping with heteroatoms is a promising approach to enhance the stability and further improve the properties of the Ag clusters.
- These atomically defined bimetallic clusters provide an ideal platform to study the effect of single-atom doping on their properties.
- Although doping effects on the electronic structures have been studied using conventional spectroscopic and electro-chemical methods, the fundamental question of how the energy levels of the superatomic orbitals are shifted upon doping has not been addressed.

Why this paper..

- Relevance to atomically precise alloy clusters and their chemistry.
- PES studies is a new area of research in these alloy nano systems, which can address some fundamental issues.
- Anion PES not only elucidate the intrinsic electronic structures of superatomic systems, but also provide insight into their photostability and photochemistry.

Photoelectron Spectroscopy (PES)

 Photoelectron spectroscopy (PES), also known as photoemission spectroscopy, refers to energy measurement of electrons emitted from solids, gases or liquids by the photoelectric effect, in order to determine the binding energies of electrons in the substance.



 Photoelectron spectroscopy in an isolated environment is a direct probe of the energy levels with respect to the vacuum level and density of states of the occupied superatomic orbitals.

Introduction

□Gas-phase PES was conducted on $[XAg_{24}(SPhMe_2)_{18}]^-$ (X=Ag, Au) and $[YAg_{24}(SPhMe_2)18]^{2-}$ (Y=Pd, Pt), which have a formal superatomic core $(X@Ag_{12})^{5+}$ or $(Y@Ag_{12})^{4+}$ with icosahedral symmetry.

□Investigation on the effect of single-atom doping on the energy levels of superatomic orbitals of $[XAg_{24}(SPhMe_2)_{18}]^-$ (X=Ag, Au) and $[YAg_{24}(SPhMe_2)_{18}]^{2^-}$ (Y=Pd, Pt) as model systems is done.

□ The gas-phase PES will provide not only fundamental information on the electronic structures of chemically modified superatoms, but also give novel insight into photoinduced electron-transport phenomena and charging energy in solution.

Experimental Setup



Figure S8. Schematic illustration of home-built apparatus for photoelectron spectroscopy. Orange and blue arrows indicate the trajectories of the ions and electrons, respectively. The solid purple arrow denotes the laser irradiation of the Nd:YAG laser.

Results



Figure 1. a) UV/Vis absorption spectra and b) ESI-TOF mass spectra of [Ag25(SR)18]-(black), [AuAg24(SR)18]- (red), [PdAg24(SR)18]2- (blue), and [PtAg24(SR)18]2-(green). Small peaks X, Y, and Z in panel (b) are assigned to the fragments [AuAg21(SPhMe2)15]-, [AuAg20(SPhMe2)14]-, and [Ag5(SPhMe2)6]-, respectively.



Figure 2. PE spectra of a) [Ag25(SR)18]-, b) [AuAg24(SR)18]-, c) [PdAg24- (SR)18]2-, and d) [PtAg24(SR)18]2- recorded at 355 nm. Insets in panels (c) and (d) are PE spectra recorded at 532 nm.



Figure 3. PE spectra of a) [Ag25(SR)18]-, b) [AuAg24(SR)18]-, c) [PdAg24-(SR)18]2-, and d) [PtAg24(SR)18]2- recorded at 266 nm.

Table 1: AEA and VDE values of the clusters, determined experimentally and calculated theoretically.

Cluster	AEA (eV)		Cluster	VDE (eV)
	Exp. (R = PhMe ₂)	Calc. (R=Me)		Calc. ^[a] (R = Me)
[Ag ₂₅ (SR) ₁₈] ⁰	$2.02\pm\!0.02$	3.46	[Ag ₂₅ (SR) ₁₈] ⁻	3.58 (3.87)
$[AuAg_{24}(SR)_{18}]^{\circ}$	2.08 ± 0.02	3.51	[AuAg ₂₄ (SR) ₁₈] ⁻	3.63 (N/A)
$[PdAg_{24}(SR)_{18}]^{-1}$	0.61 ± 0.04	1.17	[PdAg ₂₄ (SR) ₁₈] ²⁻	1.29 (1.52)
$[PtAg_{24}(SR)_{18}]^{-}$	$0.60\pm\!0.06$	1.22	$[PtAg_{24}(SR)_{18}]^{2-}$	1.34 (1.57)

[a] Calculated values obtained with the B3LYP functional are shown in parentheses. The calculation of $[AuAg_{24}(SR)_{18}]^-$ was not performed.



Figure 4. Orbital energies for a) [Ag25(SMe)18]-, b) [AuAg24(SMe)18]-, c) [PdAg24(SMe)18]2-, and d) [PtAg24(SMe)18]2-, calculated using the PBE functional. Black and red bars denote the energies of occupied and unoccupied orbitals, respectively. Orbital energies are given with reference to the calculated VDE. Table \$1. HOMO-LUMO gap theoretically calculated

Cluster	HOMO-LUMO gap (eV)		
Cluster	PBE	B3LYP	
[Ag ₂₅ (SMe) ₁₈] ⁻	1.25	2.26	
[AuAg ₂₄ (SMe) ₁₈]⁻	1.44	N.A.	
[PdAg ₂₄ (SMe) ₁₈] ²⁻	1.26	2.31	
[PtAg ₂₄ (SMe) ₁₈] ²⁻	1.42	2.50	



Figure 5. Schematic illustration of the potentials of a) $(X@Ag_{12})^{5+}(L^{-})_{6}$ (X=Ag, Au) and b) $(Y@Ag_{12})^{4+}(L^{-})_{6}$ (Y=Pd, Pt), where L denotes the Ag₂(SR)₃ staple unit. d is the distance between electron and the cluster.

Conclusion

- Using gas-phase PES, they have successfully observed how the electronic structure of [Ag₂₅(SPhMe₂)₁₈]⁻ was changed by replacing the central Ag+ with an Au+, Pt, or Pd atom.
- PES results show that superatomic orbitals in the (Au@Ag₁₂)⁵⁺ core remain unshifted with respect to those in the (Ag@Ag₁₂)⁵⁺ core, whereas the orbitals in the (Y@Ag₁₂)⁴⁺ (Y = Pd, Pt) core shift up in energy by about 1.4 eV.
- The relative energies between the energy levels were retained upon doping.

