# Non-monochromatic He I and He II UPS spectra of polycrystalline silver

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# Non-monochromatic He I and He II UPS spectra of polycrystalline silver

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## ABSTRACT

The surface composition of clean polycrystalline Silver (Ag) was analyzed by ultraviolet photoelectron spectroscopy (UPS) at optimal instrument operation parameters for both nonmonochromatic He I and He II emission. UPS valence band spectra were obtained using a differentially pumped He gas-discharge lamp (He I: 21.2 eV; He II: 40.8 eV). Fermi levels ($E_f$) in UPS spectra arising from each source line are observed—where the energy difference between $E_f$ arising from He I or He II is equivalent to the difference in source energy of He I and He II primary lines (19.6 eV), useful for calibration of UPS systems or spectra analysis.

**Key words:** UPS, He I, He II, silver, Ag



**Accession #:** 01731
**Technique:** XPS, UPS
**Host Material:** Ag
**Instrument:** ScientaOmicron ESCA2SR
**Major Elements in Spectra:** Ag
**Minor Elements in Spectra:** None
**Published Spectra:** 4
**Spectra in Electronic Record:** 4
**Spectral Category:** Reference

## INTRODUCTION

Ultraviolet photoelectron spectroscopy (UPS) has proven to be an effective technique to detect and describe the properties of a material's work function (Refs. 1–4), oxidation states (Refs. 5 and 6), surface adsorption or modification by molecular species (Refs. 7–10), and chemical bonding domains (Refs. 11–13). Helium-UPS probes valence electronic states with a much higher surface sensitivity than XPS, by reason of the primary He ionization source transitions being lower in KE (He I: 21.2 eV; He II: 40.8 eV) (Refs. 14 and 15). Due to the conservation of momentum, UPS only provides a partial density-of-states, having access to two energies allows one to vary the intensities of the lower and higher momentum orbitals, which aids orbital identification (Ref. 16). Although one specific He source line (He I or He II) can be selected for by control of gas-discharge lamp operation parameters, the other lines remain present in the source emission. This means that although a gas-discharge He UPS source may be set to operate at optimized parameters for maximizing emission of a specific He line, collected spectra will still show photoemission peaks originating from other He lines leaving the source, at ratios depending on the set operation parameters. The identification of these extra spectral lines has been overlooked in the UPS literature in the past. In this sense, we find that using polycrystalline Ag as a standard example for differentiation of He I and He II lines from a non-monochromatic source is beneficial. Included spectra are XPS survey, high-resolution, and UPS valence bands collected at optimized gas-discharge operation conditions for maximizing emission of either He I or He II source lines. Regions in the Ag valence band are composed of 4*d* and 5*s* orbitals and have been labeled as such in the UPS spectra.

## SPECIMEN DESCRIPTION (ACCESSION # 01731)

**Host Material:** Silver
**CAS Registry #:** 7440-22-4
**Host Material Characteristics:** Homogeneous; solid; polycrystalline; conductor; metal; other
**Chemical Name:** Silver
**Source:** ScientaOmicron

**Host Composition:** Ag
**Form:** Pressed pellet
**Structure:** Ag
**History and Significance:** Calibration standard supplied by the instrument manufacturer
**As Received Condition:** Pure
**Analyzed Region:** Valence band
***Ex Situ* Preparation/Mounting:** Mounted onto a grounded stage
***In Situ* Preparation:** Ion etching for surface cleaning
**Charge Control:** None
**Temp. During Analysis:** 293 K
**Pressure During Analysis:** $6.5 \times 10^{-6}$ Pa
**Pre-analysis Beam Exposure:** 15 s

## INSTRUMENT DESCRIPTION

**Manufacturer and Model:** ScientaOmicron ESCA 2SR
**Analyzer Type:** Spherical sector
**Detector:** Multichannel resistive plate
**Number of Detector Elements:** 128

## INSTRUMENT PARAMETERS COMMON TO ALL SPECTRA

### Spectrometer

**Analyzer Mode:** Constant pass energy
**Throughput ($T = E^N$):** N = 0
**Throughput comment:** As provided by the vendor, the input lens is operated in a way that the throughput of the analyzer is a function of the retard ratio only.
**Excitation Source Window:** None
**Excitation Source:** Al $K_\alpha$ monochromatic, He I, He II
**Source Energy:** eV
**Source Strength:** XPS: 300; He I: 52.9; He II: 89.4 W
**Source Beam Size:** XPS:$2000 \times 2000\,\mu m^2$; UPS: $4000 \times 4000\,\mu m^2$
**Signal Mode:** Multichannel direct

### Geometry

**Incident Angle:** 54.7°
**Source-to-Analyzer Angle:** 54.7°
**Emission Angle:** 0°
**Specimen Azimuthal Angle:** 90°
**Acceptance Angle from Analyzer Axis:** 0°
**Analyzer Angular Acceptance Width:** ±9.0°

### Ion Gun

**Manufacturer and Model:** FOCUS FDG 150
**Energy:** 4000 eV
**Current:** $3.2\,\mu A$
**Current Measurement Method:** Faraday cup
**Sputtering Species:** Ar
**Spot Size (unrastered):** $150\,\mu m$
**Raster Size:** $4000 \times 4000\,\mu m^2$
**Incident Angle:** 45°
**Polar Angle:** 45°
**Azimuthal Angle:** 27.5°
**Comment:** Differentially pumped ion source

## DATA ANALYSIS METHOD

**Energy Scale Correction:** The binding energy scale was referenced to Ag $3d_{5/2} = 368.2$ eV.
**Recommended Energy Scale Shift:** 0
**Peak Shape and Background Method:** Voigt profile (GL 70), Shirley background
**Quantitation Method:** Quantification and data analysis was done using CASAXPS version 2.3.24.

## ACKNOWLEDGMENTS

This work made use of the Cornell Center for Materials Research Shared Facilities, which are supported through the NSF MRSEC program (No. DMR-1719875). We thank Dr. Justin Gorham, Dr. Craig Perkins, and Dr. Darrah Dare for their insightful discussions.

## AUTHOR DECLARATIONS

### Conflict of Interest

The authors have no conflicts to disclose.

### Author Contributions

M.G.S. and J.C. contributed equally to this work.

## DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material (Ref. 17).

## REFERENCES

[1]B. Bröker *et al.*, Appl. Phys. **93**, 243303 (2008).
[2]E. R. Kötz, H. Neff, and K. Müller, J. Electroanal. Chem. Interf. Electrochem. **215**, 331 (1986).
[3]M. Shiraishi and M. Ata, Carbon **39**, 1913 (2001).
[4]D. R. Baer, R. L. Gordon, and C. W. Hubbard, Appl. Surf. Sci. **45**, 71 (1990).
[5]Y. Enta, Y. Takegawa, M. Suemitsu, and N. Miyamoto, Appl. Surf. Sci. **100–101**, 449 (1996).
[6]M. Heber and W. Grünert, J. Phys. Chem. **104**, 5288 (2000).
[7]C. R. Brundle and A. F. Carley, Faraday Discuss. Chem. Soc. **60**, 51 (1975).
[8]T. E. Felter, W. H. Weinberg, G. Y. Lastushkina, A. I. Boronin, P. A. Zhdan, G. K. Boreskov, and J. Hrbek, Surf. Sci. **118**, 369 (1982).
[9]S. Yashonath, P. K. Basu, A. Srinivasan, M. S. Hedge, and C. N. R. Rao, Proc. Indian Acad. Sci. **91**, 101 (1982).
[10]I. Kojima, M. Orita, E. Miyazaki, and S. Otani, Surf. Sci. **160**, 153 (1985).
[11]M. Salim, J. Hurst, M. Montgomery, N. Tolman, and H. Liu, J. Electron Spectrosc. Relat. Phenom. **235**, 8 (2019).
[12]M. Keil *et al.*, J. Phys. Chem. **104**, 3967 (2000).
[13]W. R. Salaneck, J. Electron Spectrosc. Relat. Phenom. **174**, 3 (2009).
[14]D. W. Turner, Philos. Trans. Royal Soc. A **268**, 7 (1970).
[15]D. W. Turner and M. I. A. Jobory, J. Chem. Phys. **37**, 3007 (1962).
[16]J. J. Yeh and I. Lindau, At. Data Nucl. Data Tables **32**, 1 (1985).
[17]See supplementary material at https://doi.org/10.1116/6.0001569 for data files of the spectra provided in this study.

**SPECTRAL FEATURES TABLE**

| Spectrum ID # | Element/ Transition | Peak Energy[a] (eV) | Peak Width FWHM[b] (eV) | Peak Area (eV×counts/s) | Sensitivity Factor | Concentration (at. %) | Peak Assignment |
|---|---|---|---|---|---|---|---|
| 01731-01 | Ag | … | … | … | … | 100 | … |
| 01731-03 | Ag | 40.8 | 0.16 | … | … | … | $E_f$ (He I) |
| 01731-03 | Ag | 21.2 | 0.13 | … | … | … | $E_f$ (He II) |

[a]Peak energy is reported as kinetic energy.
[b]FWHM is reported as the 12%–88% width of the Fermi edge.

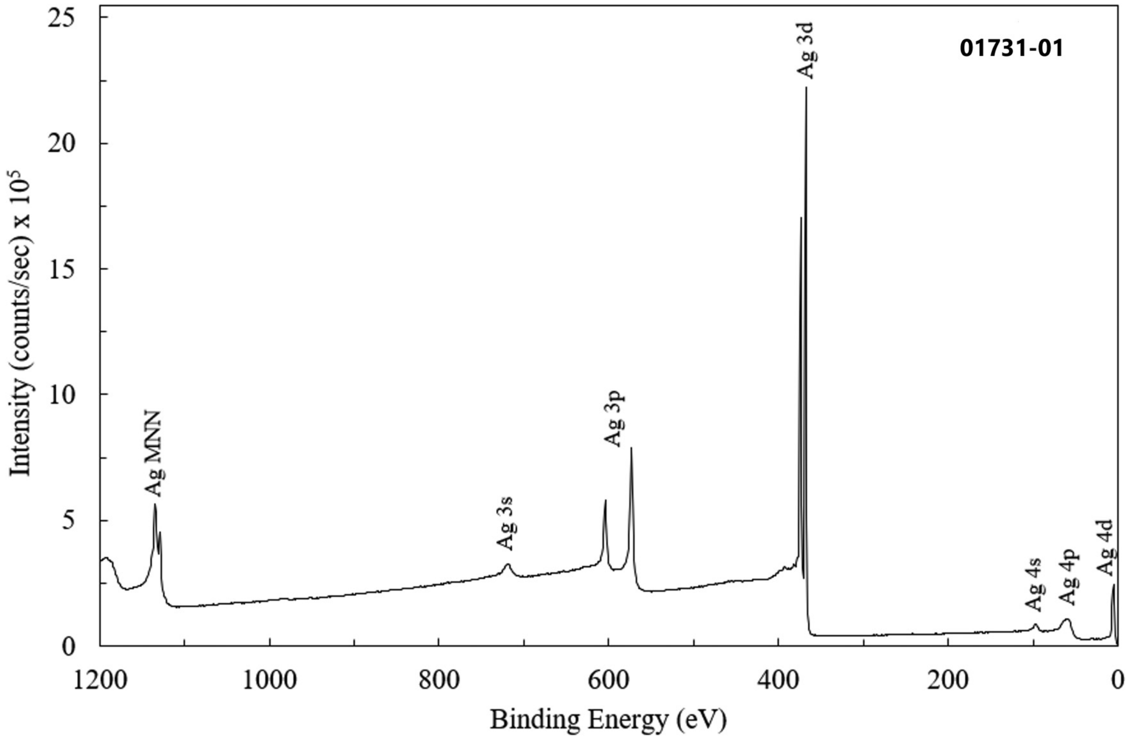
**ANALYZER CALIBRATION TABLE**

| Spectrum ID # | Element/ Transition | Peak Energy (eV) | Peak Width FWHM (eV) | Peak Area (eV×counts/s) | Sensitivity Factor | Concentration (at. %) | Peak Assignment |
|---|---|---|---|---|---|---|---|
| 01731-02 | Ag $3d_{5/2}$ | 368.2 | 0.67 | 523 849.8 | … | … | … |

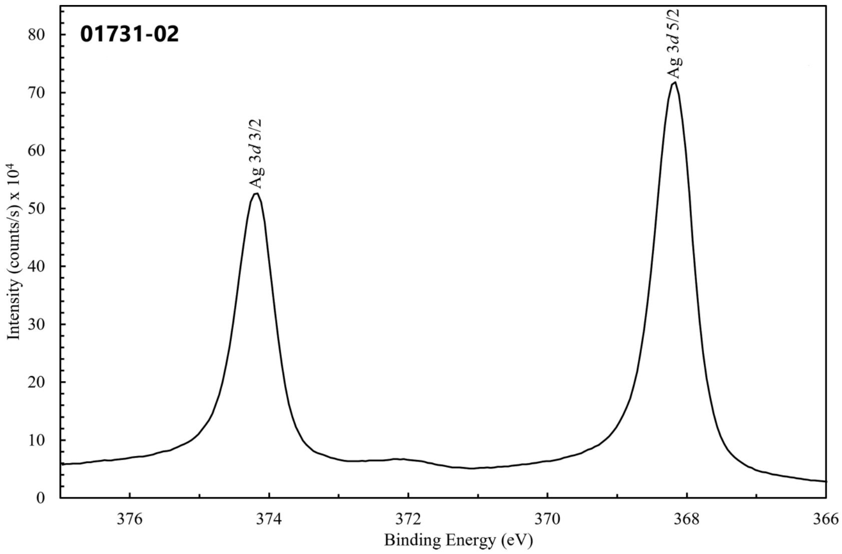
**GUIDE TO FIGURES**

| Spectrum (Accession) # | Spectral Region | Voltage Shift | Multiplier | Baseline | Comment # |
|---|---|---|---|---|---|
| 01731-01 | Survey | 0 | 1 | 0 | 1 |
| 01731-02 | Ag 3d | 0 | 1 | 0 | 2 |
| 01731-03 | Valence band | 0 | 1 | 0 | 3 |
| 01731-04 | Valence band | 0 | 1 | 0 | 4 |

1. Monochromated Al $K_\alpha$ source.
2. Monochromated Al $K_\alpha$ source.
3. Differentially pumped He gas-discharge UPS source optimized for He II emission (operation parameters: 200 mA; 447 V; $2.3 \times 10^{-2}$ mBar in the first pumping stage).
4. Differentially pumped He gas-discharge UPS source optimized for He I emission (operation parameters: 100 mA; 529 V; $9.2 \times 10^{-2}$ mBar in the first pumping stage).

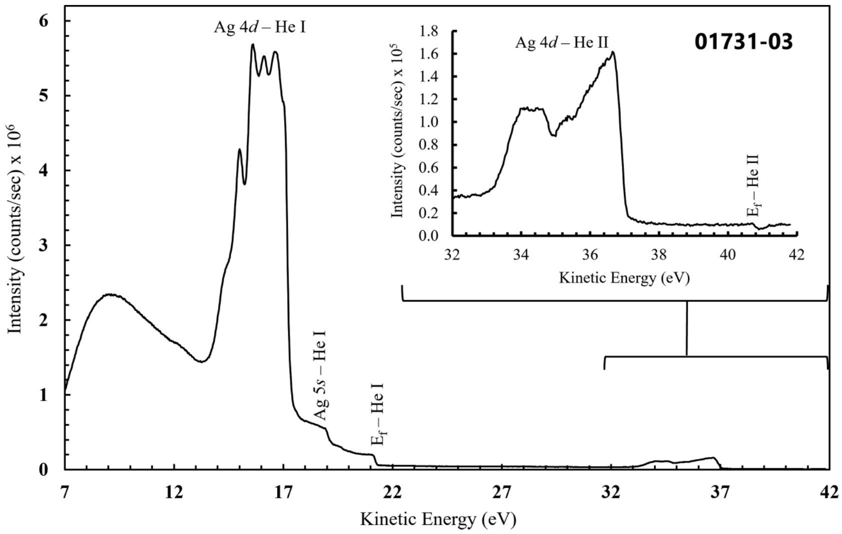



| Accession # | 01731-01 |
|---|---|
| **Host Material:** | Ag |
| **Technique:** | XPS |
| **Spectral Region:** | Survey |
| **Instrument:** | ScientaOmicron ESCA2SR |
| **Excitation Source:** | Al $K_{\alpha}$ monochromatic |
| **Source Energy:** | 1487.6 eV |
| **Source Strength:** | 300 W |
| **Source Size:** | 2 × 2 $mm^2$ |
| **Analyzer Type:** | Spherical sector analyzer |
| **Incident Angle:** | 54.7° |
| **Emission Angle:** | 0° |
| **Analyzer Pass Energy:** | 200 eV |
| **Analyzer Resolution:** | 0.219 eV |
| **Total Signal Accumulation Time:** | 240 s |
| **Total Elapsed Time:** | 240 s |
| **Number of Scans:** | 2 |
| **Effective Detector Width:** | 28 eV |



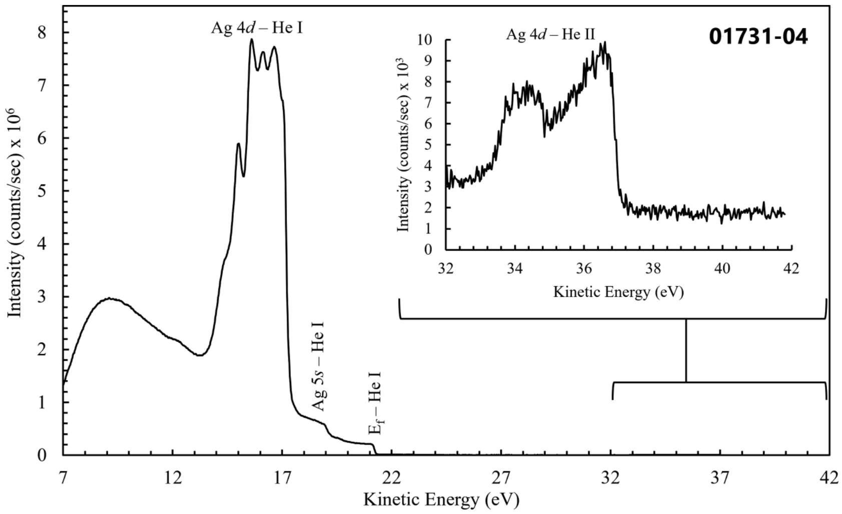

- **Accession #:** 01731-02
- **Host Material:** Ag
- **Technique:** XPS
- **Spectral Region:** Ag 3d

Instrument: ScientaOmicron ESCA2SR
Excitation Source: Al $K_{\alpha}$ monochromatic
Source Energy: 1487.6 eV
Source Strength: 300 W
Source Size: 2 × 2 $mm^2$
Analyzer Type: Spherical sector
Incident Angle: 54.7°
Emission Angle: 0°
Analyzer Pass Energy: 52 eV
Analyzer Resolution: 0.057 eV
Total Signal Accumulation Time: 45 s
Total Elapsed Time: 45 s
Number of Scans: 1
Effective Detector Width: 7.28 eV




- **Accession #:** 01731-03
- **Host Material:** Ag
- **Technique:** UPS
- **Spectral Region:** Valence band

Instrument: ScientaOmicron—HIS 13
Excitation Source: He II
Source Energy: 40.8 eV
Source Strength: 89.4 W
Source Size: 4 × 4 $mm^2$
Analyzer Type: Spherical sector
Incident Angle: 45°
Emission Angle: 0°
Analyzer Pass Energy: 10 eV
Analyzer Resolution: 0.105 eV
Total Signal Accumulation Time: 280 s
Total Elapsed Time: 280 s
Number of Scans: 1
Effective Detector Width: 1.4 eV




- **Accession #:** 01731-04
- **Host Material:** Ag
- **Technique:** UPS
- **Spectral Region:** Valence band

Instrument: ScientaOmicron—HIS 13
Excitation Source: He I
Source Energy: 21.2 eV
Source Strength: 52.9 W
Source Size: 4 × 4 $mm^2$
Analyzer Type: Spherical sector
Incident Angle: 45°
Emission Angle: 0°
Analyzer Pass Energy: 10 eV
Analyzer Resolution: 0.105 eV
Total Signal Accumulation Time: 280 s
Total Elapsed Time: 280 s
Number of Scans: 1
Effective Detector Width: 1.4 eV