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HAXPES reference spectra of MoS₂ with Cr K_α excitation

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(Received day Month year; accepted day Month year; published day Month year)

Monochromatic Cr K_α radiation (5414.8 eV) was used to acquire high-energy photoelectron spectroscopy (HAXPES) data on pure bulk MoS₂. The reported spectra include a survey scan, high-resolution spectra of Mo 2s, Mo 2p, Mo 3s, Mo 3p, Mo 3d, Mo 4s, Mo 4p, S 1s, S 2p, and S 2s core-levels and X-ray excited Auger spectra. The data will be useful for HAXPES studies of Mo compounds.

Keywords: MoS₂, HAXPES, Cr K_α

INTRODUCTION

Recently developed laboratory based hard x-ray photoelectron spectrometers (HAXPES) allow to excite deeper core-levels, enabling different depth probing as a function of the studied core-level. In the case of MoS₂, Cr K_α radiation (5414.8 eV) allows to ionize all Mo and S core-levels of principal quantum numbers N=2, 3 and 4.

In this work, we report HAXPES spectra recorded on a pure, bulk MoS₂ sample. MoS₂ is widely used in mechanics and wear science, electronics and phototonics, as well as in chemistry and catalysis. In HAXPES this material has already been studied with Ag L_α X-rays (2984.2 eV) (Ref 1) and with synchrotron radiation hard X-rays (5.9 keV) (Ref 2) with a focus on the band alignment and the low energy core levels. The present data include a survey scan, high-resolution Mo 2s, Mo 2p, Mo 3s, Mo 3p, Mo 3d, Mo 4s, Mo 4p, S 1s, S 2p, and S 2s core-levels, and X-ray excited Auger spectra.

SPECIMEN DESCRIPTION (ACCESSION # 01987)

Specimen: MoS₂

CAS Registry #: 1317-33-5

Specimen Characteristics: homogeneous; solid; polycrystalline; semiconductor; inorganic compound; other

Chemical Name: Molybdenum disulfide

Source: HQ Graphene

Composition: MoS₂

Form: Polycrystalline solid

Structure: Hexagonal, layered structure

History & Significance: Air exposed thick MoS₂ sample

As Received Condition: Bulk MoS₂ crystal

Analyzed Region: Same as specimen

Ex Situ Preparation/Mounting: The sample was mounted on the sample holder using double sided conductive tape.

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Accession#: 01987

Technique: XPS, XAES

Specimen: MoS₂

Instrument: ULVAC-PHI Quantes

Major Elements in Spectra: Mo, S

Minor Elements in Spectra: O, Cl

Published Spectra: 12

Spectral Category: Reference

In Situ Preparation: None

Charge Control: Low-energy electrons (1 eV, filament 1.1 A) and low-energy Ar⁺ ions (100 eV)

Temp. During Analysis: 300 K

Pressure During Analysis: < 2 x 10⁻⁷ Pa

Pre-analysis Beam Exposure: 0 s

INSTRUMENT DESCRIPTION

Manufacturer and Model: ULVAC-PHI Quantes

Analyzer Type: spherical sector

Detector: multichannel plate resistive

Number of Detector Elements: 32

INSTRUMENT PARAMETERS COMMON TO ALL SPECTRA

■ Spectrometer

Analyzer Mode: constant pass energy

Throughput (T=E^N): The energy dependence can be modeled using the following equation: $\frac{A}{E_p} = \left(\frac{a^2}{a^2 + R^2}\right)^b$, where a and b are constants, E_p is the pass energy, A is the peak area and R is the retard ratio equal to E/E_p, where E is the kinetic energy. Three spectral regions are recorded on a sputter cleaned sample (Cu, Ag, Au) at different pass energies. The values of a and b are then determined by a linear least square fit of the data applying the equation described above.

Excitation Source Window: Al

Excitation Source: Cr K_α monochromatic

Source Energy: 5414.8 eV

Source Strength: 45 W

Source Beam Size: 100 x 100 μm²

Signal Mode: multichannel direct

■ Geometry

Incident Angle: 22 °

Source-to-Analyzer Angle: 46 °
Emission Angle: 45 °
Specimen Azimuthal Angle: 0 °
Acceptance Angle from Analyzer Axis: 0 °
Analyzer Angular Acceptance Width: 20 ° x 20 °

■ Ion Gun

Manufacturer and Model: ULVAC-PHI Quantex
Energy: 100 and 2000 eV
Current: 0.001 mA
Current Measurement Method: Faraday cup
Sputtering Species and Charge: Ar⁺
Spot Size (unrastered): 100 μm
Raster Size: 3000 x 3000 μm²
Incident Angle: 45 °
Polar Angle: 45 °
Azimuthal Angle: 45 °

Comment: Differentially pumped ion gun used for pre-sputtering of the sample and to prevent reoxidation during analysis.

DATA ANALYSIS METHOD

Energy Scale Correction: The decrease of photoionization cross-sections in HAXPES (Refs. 3 and 4) leads to a very low C 1s intensity. Therefore, the binding energy was referenced to the S 2p binding energy position measured with Al K_α radiation after shifting the C 1s peak to 284.8 eV. Doing so, the S 2p binding energy was 162.4 eV. The HAXPES spectra were then rescaled by shifting the S 2p to 162.4 eV. This correction sets the Mo 3d_{5/2} binding energy to 228.8 eV, in line with a previous study (Ref 5) and in the range of reported values by NIST (Ref 6).

Recommended Energy Scale Shift: -0.4 eV for binding energy

Peak Shape and Background Method: Shirley background was employed for peak area determination. No curve fitting was performed on the spectra. The Auger peaks were identified using previous work on H₂S and PHI Handbook (ref 7 and 8).

Quantitation Method: PHI Multipak software Version 9.9.0.8 was used to perform quantitation of bulk MoS₂. An XPS quantification conducted on the same sample, considering Mo 3d and S 2p core-levels, gives a 1:1.97 Mo:S ratio. The determined HAXPES intensities were checked for repeatability by comparing, before and after acquisition, the intensity of the Ag 3d and Ag 2p_{3/2} line of a sputter-clean, bulk silver sample mounted on the same holder. In all cases the standard deviation in intensity was below 4%. Empirically determined sensitivity factors (RSFs) were provided by Multipak. The RSFs were derived from the pure-element relative sensitivity factor as defined in ISO 18118:2015 (Ref 9) which were measured on pure element samples using a Cr K_α source. They therefore account for the decrease of cross-section and different escape depths of photoelectrons using higher energy photons. RSFs are reported proportional to the RSF of F 1s equal to 1. Corrected RSFs including the spectrometer transmission function and asymmetry parameter of the considered core-line were used to calculate the concentrations. The area used for the quantification and reported in the Spectral Feature Table was measured over the entire energy

range of presented spectra. For instance, the S 1s area includes the small peak around 2480 eV. As shown in the Spectral Feature Table, the percentage of deviation relative to the nominal 1:2 Mo:S ratio depends on the considered core-levels and is up to -45%, with some combinations providing the expected figure. A more detailed HAXPES study is necessary to improve quantitation results of this material.

ACKNOWLEDGMENTS

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AUTHOR DECLARATIONS

Conflicts of Interest (required)

The authors have no conflict to disclose.

DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available within the article and its supplementary material.

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determined relative sensitivity factors for the quantitative analysis of homogeneous materials, ISO 18118:2015.

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SPECTRAL FEATURES TABLE							
Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV x cts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
01987-02	S 1s	2469.8	1.33	8982	6.068	63.7 (vs Mo 2p _{1/2})	MoS ₂
01987-03	S 2s	229.1	1.05	502	0.601	...	S
01987-04	S 2p	162.0	1.89	388	0.252 ^b	50.3 (vs Mo 4p)	S
01987-05	Mo 2s	2868.0	4.10	4287	3.805	...	MoS ₂
01987-06	Mo 2p _{3/2}	2522.3	2.19	10295	9.584	...	Mo
01987-07	Mo 2p _{1/2}	2627.0	2.2	4895	4.969	36.3 (vs S 1s)	Mo
01987-08	Mo 3s	506.67	6.22	1145	0.971	...	Mo
01987-09	Mo 3p _{3/2}	395.0	2.58	2131	2.063	...	Mo
01987-09	Mo 3p _{1/2}	412.5	2.56	915	1.134	...	Mo
01987-03	Mo 3d _{3/2}	232.30	1.21	334	1.103	...	Mo
01987-03	Mo 3d _{5/2}	226.30	1.76	408	1.103	...	Mo
01987-10	Mo 4s	63.17	5.45	489	0.284	...	Mo
01987-11	Mo 4p	36.70	3.60	479	0.425 ^b	49.7 (vs S 2p)	Mo
01987-12 ^a	Mo LMM	2037.2
01987-12 ^a	Mo LMM	2142.0
01987-12 ^a	Mo LMM	1852.7
01987-12 ^a	Mo LMM	1874.3
01987-12 ^a	S KLL	2044.2
01987-12 ^a	S KLL	2115.9

^a Peak energy reported as kinetic energy.

^b Uncertain value

ANALYZER CALIBRATION TABLE							
Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV x cts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
...	Ag 3d _{5/2}	368.12	0.63	114999
...	Cu 2p _{3/2}	932.61	0.96	40205
...	Au 4f _{7/2}	83.89	0.78	100500

Comment to Analyzer Calibration Table: The spectra in the analyzer calibration table were recorded using Al K_α photons.

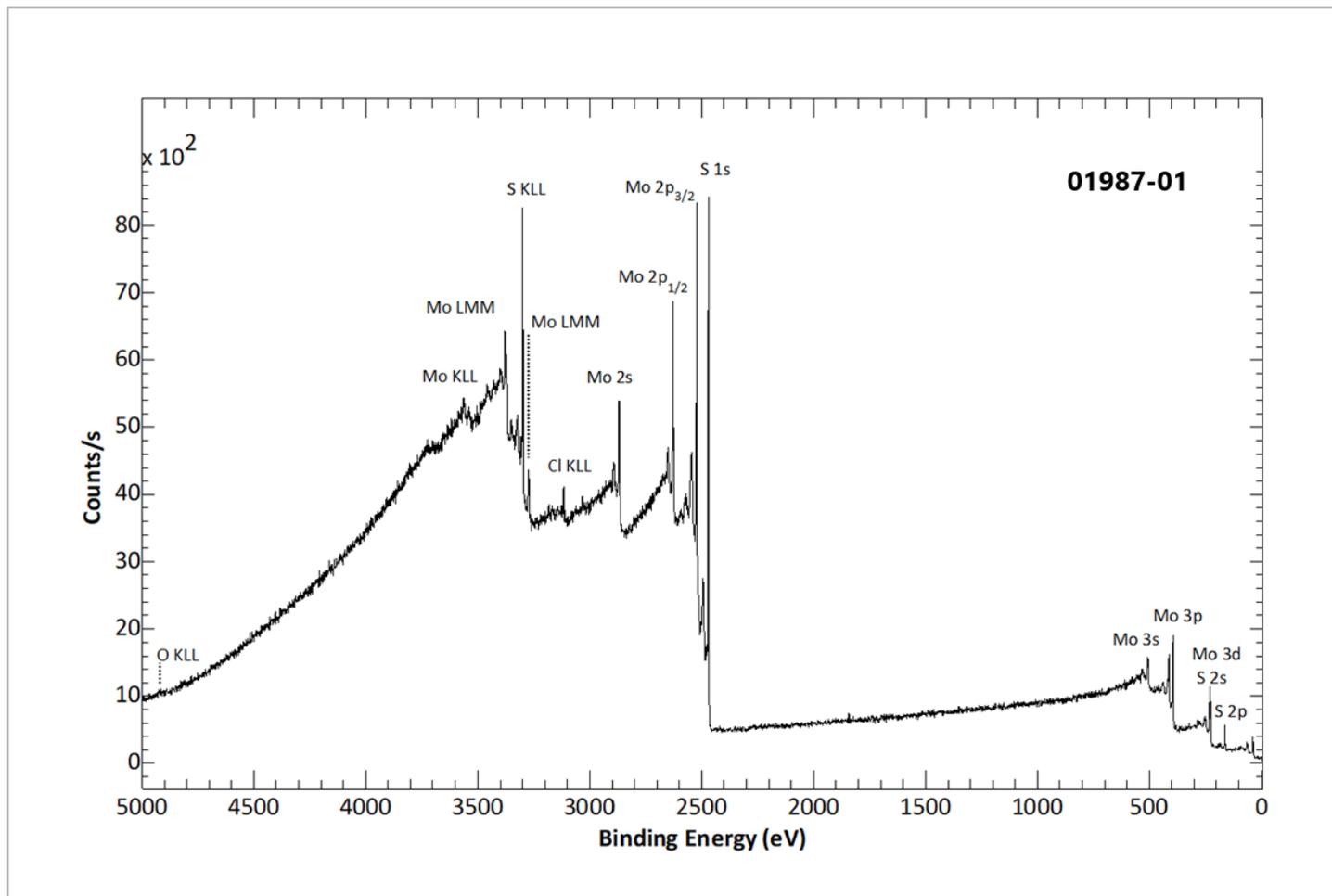
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GUIDE TO FIGURES					
Spectrum ID #	Element/ Transition	Voltage Shift*	Multiplier	Baseline	Comment #
01987-01	Survey	0	1	0	...
01987-02	S 1s	+0.4	1	0	...
01987-03	S 2s / Mo 3d	+0.4	1	0	...
01987-04	S 2p	+0.4	1	0	...
01987-05	Mo 2s	+0.4	1	0	...
01987-06	Mo 2p _{3/2}	+0.4	1	0	...
01987-07	Mo 2p _{1/2}	+0.4	1	0	...
01987-08	Mo 3s	+0.4	1	0	...
01987-09	Mo 3p	+0.4	1	0	...
01987-10	Mo 4s	+0.4	1	0	...
01987-11	Mo 4p	+0.4	1	0	...
01987-12	Mo KLL, Mo LMM, S KLL, Mo LMM	0	1	0	...

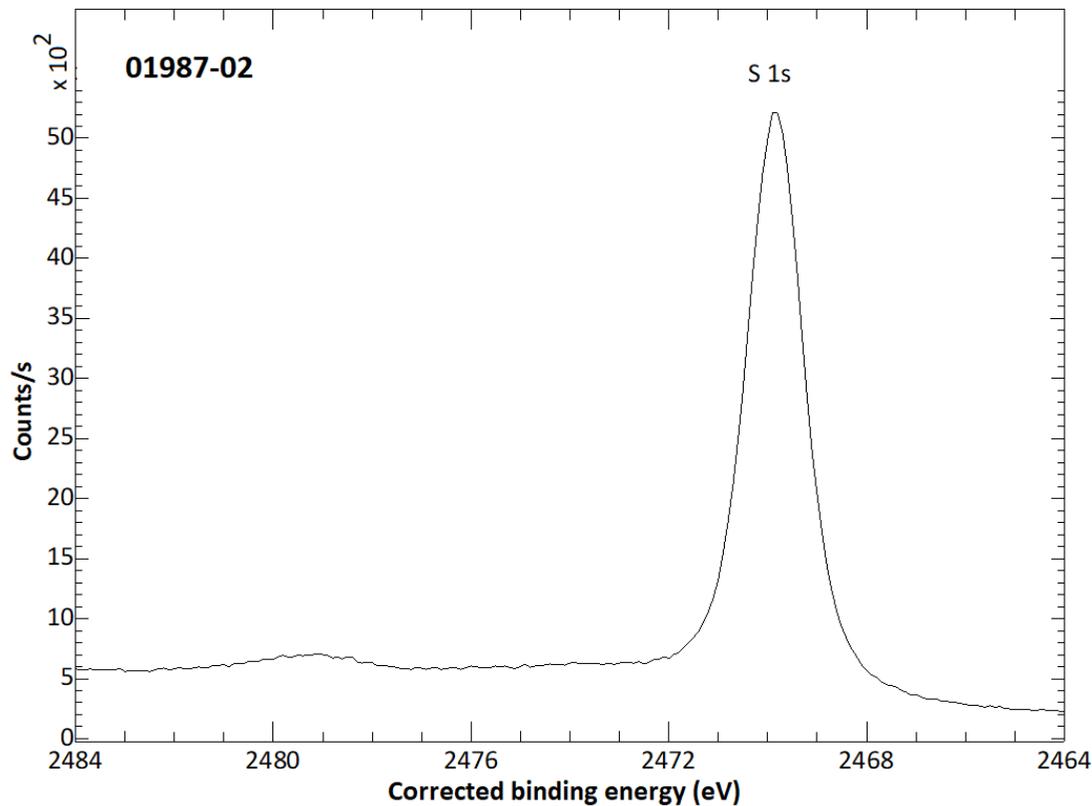
*Voltage shift of the archived (as-measured) spectrum relative to the printed figure. The figure reflects the recommended energy scale correction due to a calibration correction, sample charging, flood gun, or other phenomenon.

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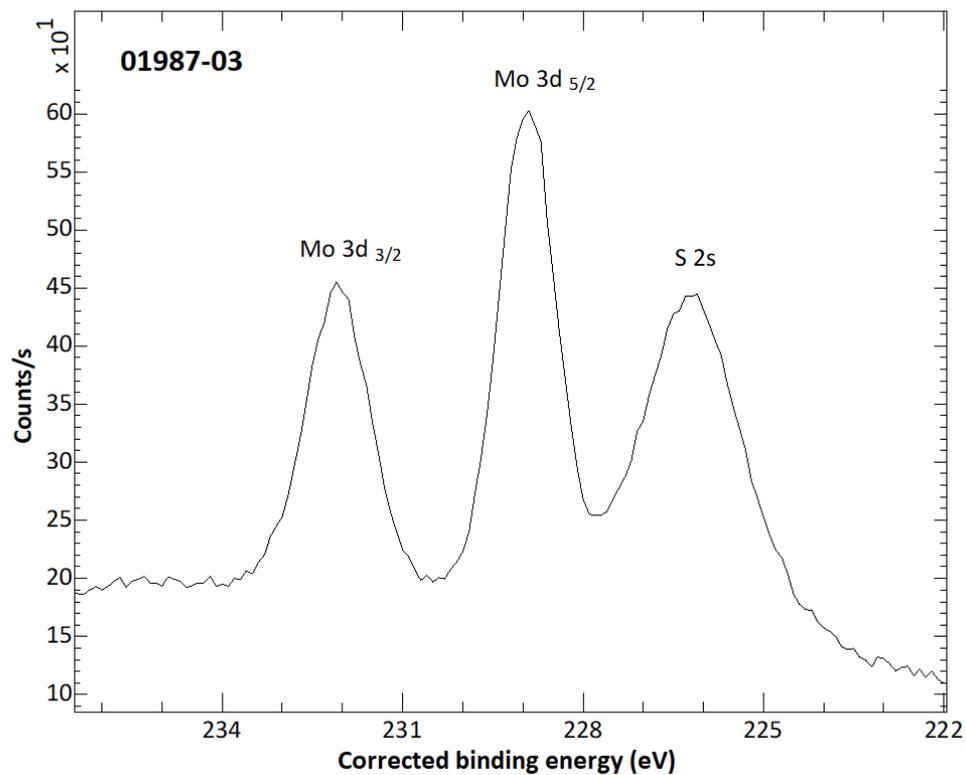


Accession #	01987-01
■ Specimen	MoS ₂
■ Technique	XPS
■ Spectral Region	Survey
Instrument	ULVAC-PHI Quantes
Excitation Source	Cr K _α monochromatic
Source Energy	5414.8 eV
Source Strength	45 W
Source Size	100 x 100 μm ²
Analyzer Type	spherical sector analyzer
Incident Angle	22°
Emission Angle	45°
Analyzer Pass Energy	280 eV
Instrument Resolution	2.33 eV
Total Signal Accumulation Time	8058 s
Total Elapsed Time	8868 s
Number of Scans	8

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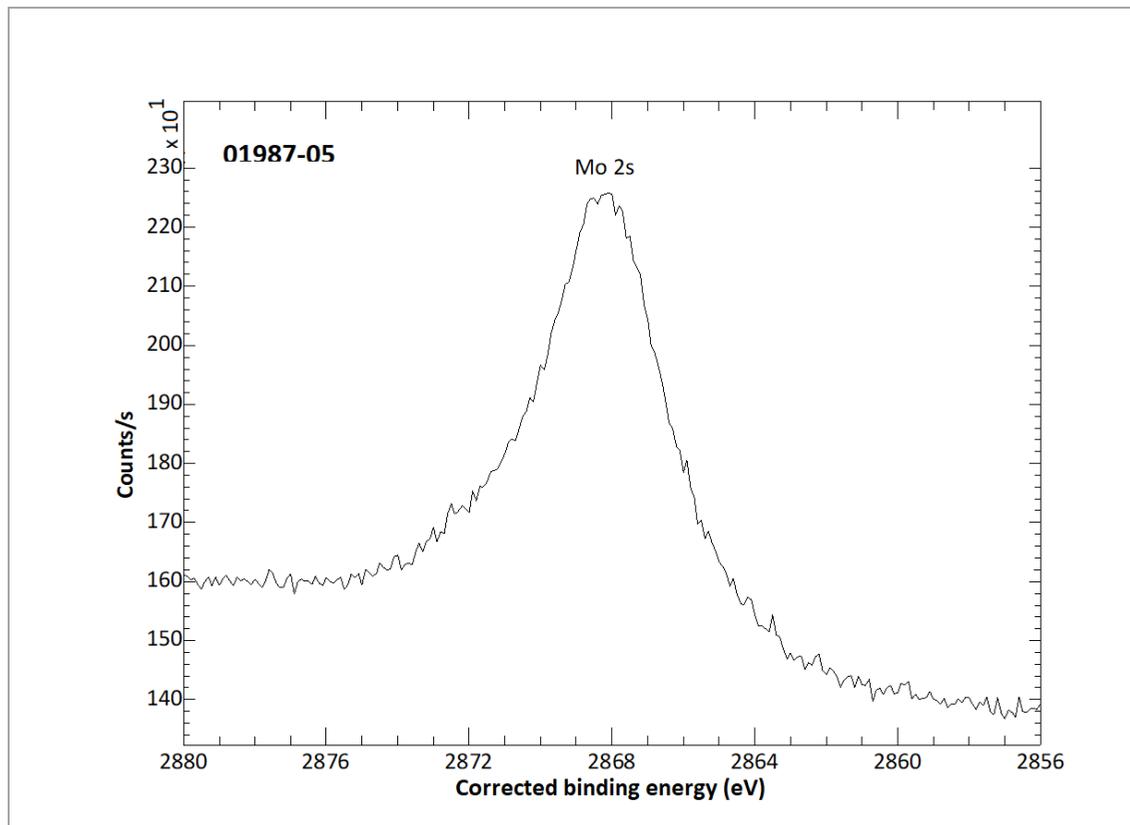


■ **Accession #:** 01987-02
 ■ **Specimen:** MoS₂
 ■ **Technique:** XPS
 ■ **Spectral Region:** S 1s
 Instrument: ULVAC-PHI Quantes
 Excitation Source: Cr K_α monochromatic
 Source Energy: 5414.8 eV
 Source Strength: 45 W
 Source Size: 100 × 100 μm²
 Analyzer Type: spherical sector
 Incident Angle: 22 °
 Emission Angle: 45 °
 Analyzer Pass Energy 112 eV
 Instrument Resolution: 1.17 eV
 Total Signal Accumulation Time: 3108 s
 Total Elapsed Time: 3426 s
 Number of Scans: 24

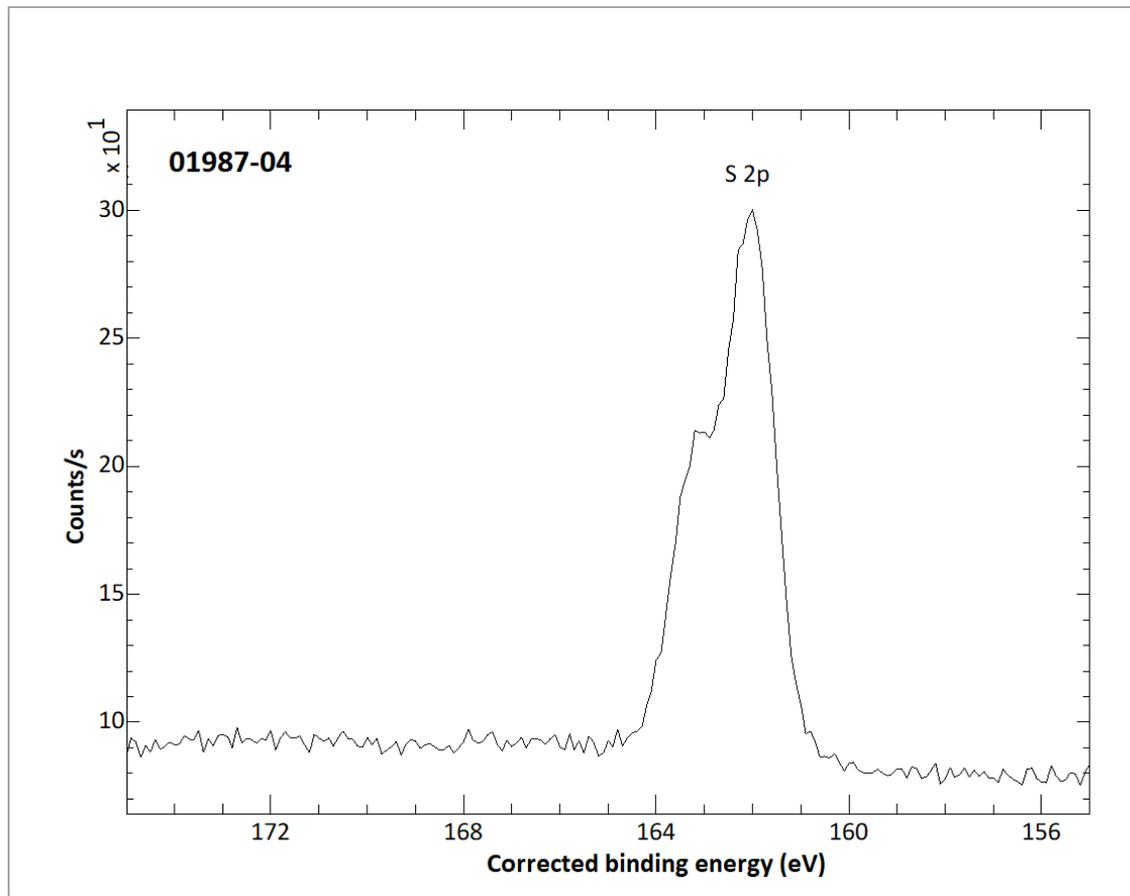


■ **Accession #:** 01987-03
 ■ **Specimen:** MoS₂
 ■ **Technique:** XPS
 ■ **Spectral Region:** S 2s / Mo 3d
 Instrument: ULVAC-PHI Quantes
 Excitation Source: Cr K_α monochromatic
 Source Energy: 5414.8 eV
 Source Strength: 45 W
 Source Size: 100 × 100 μm²
 Analyzer Type: spherical sector
 Incident Angle: 22 °
 Emission Angle: 45 °
 Analyzer Pass Energy 112 eV
 Instrument Resolution: 1.17 eV
 Total Signal Accumulation Time: 6222 s
 Total Elapsed Time: 6858 s
 Number of Scans: 48

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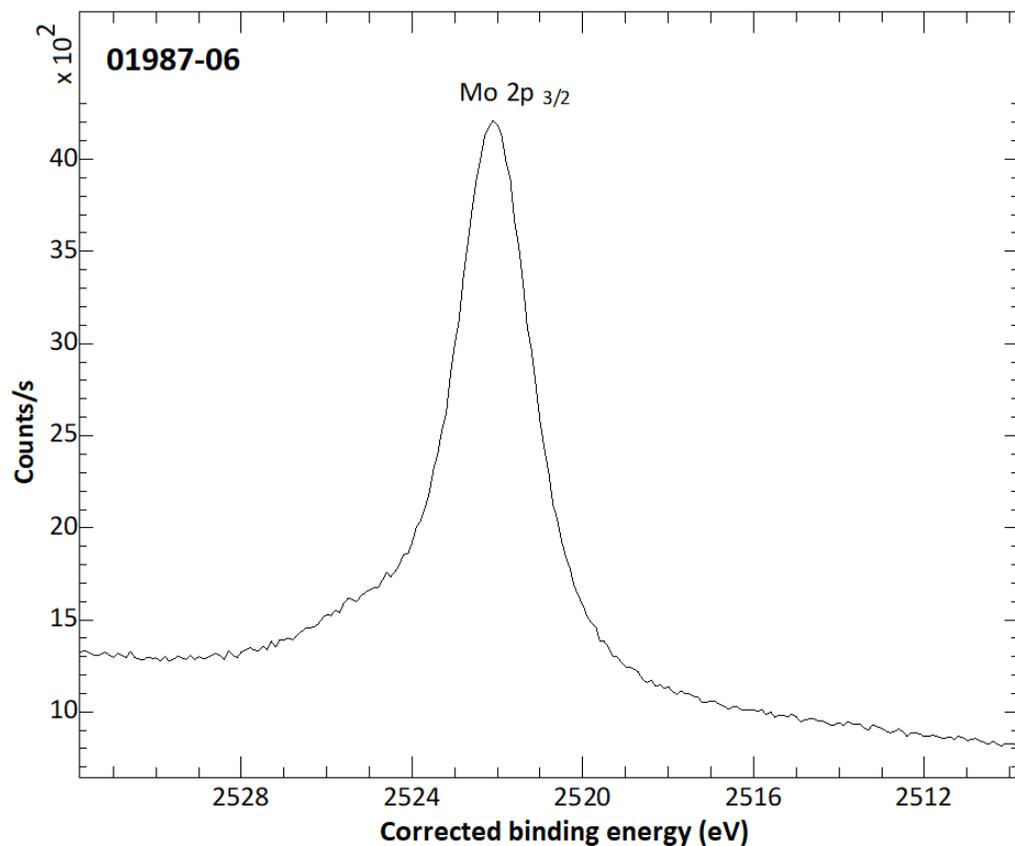


■ **Accession #:** 01987-05
 ■ **Specimen:** MoS₂
 ■ **Technique:** XPS
 ■ **Spectral Region:** Mo 2s
 Instrument: ULVAC-PHI Quantes
 Excitation Source: Cr K_α monochromatic
 Source Energy: 5414.8 eV
 Source Strength: 45 W
 Source Size: 100 × 100 μm²
 Analyzer Type: spherical sector
 Incident Angle: 22 °
 Emission Angle: 45 °
 Analyzer Pass Energy 112 eV
 Instrument Resolution: 1.17 eV
 Total Signal Accumulation Time: 5244 s
 Total Elapsed Time: 5778 s
 Number of Scans: 36

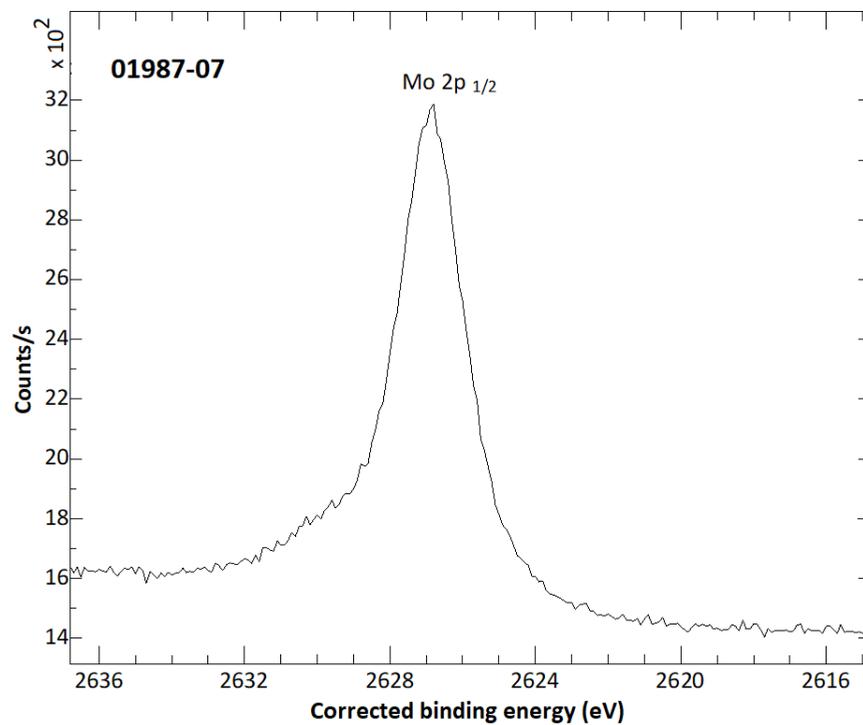


■ **Accession #:** 01987-04
 ■ **Specimen:** MoS₂
 ■ **Technique:** XPS
 ■ **Spectral Region:** S 2p
 Instrument: ULVAC-PHI Quantes
 Excitation Source: Cr K_α monochromatic
 Source Energy: 5414.8 eV
 Source Strength: 45 W
 Source Size: 100 × 100 μm²
 Analyzer Type: spherical sector
 Incident Angle: 22 °
 Emission Angle: 45 °
 Analyzer Pass Energy 112 eV
 Instrument Resolution: 1.17 eV
 Total Signal Accumulation Time: 6222 s
 Total Elapsed Time: 6858 s
 Number of Scans: 48

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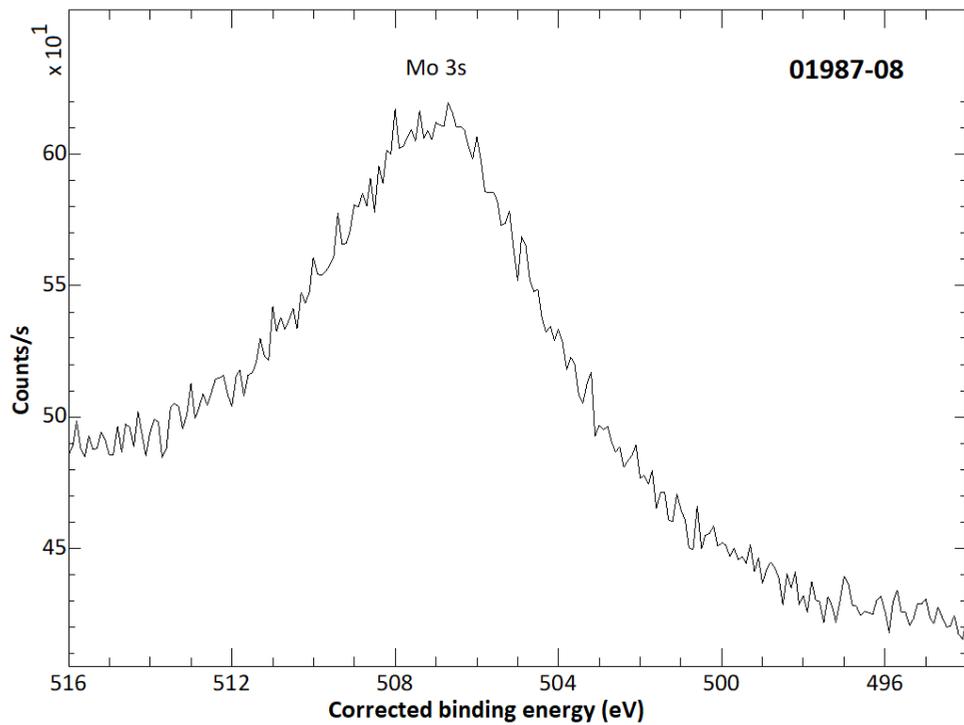


■ Accession #: 01987-06
 ■ Specimen: MoS₂
 ■ Technique: XPS
 ■ Spectral Region: Mo 2p_{3/2}
 Instrument: ULVAC-PHI Quantes
 Excitation Source: Cr K_α monochromatic
 Source Energy: 5414.8 eV
 Source Strength: 45 W
 Source Size: 100 × 100 μm²
 Analyzer Type: spherical sector
 Incident Angle: 22 °
 Emission Angle: 45 °
 Analyzer Pass Energy 112 eV
 Instrument Resolution: 1.17 eV
 Total Signal Accumulation Time: 3300 s
 Total Elapsed Time: 3642 s
 Number of Scans: 24

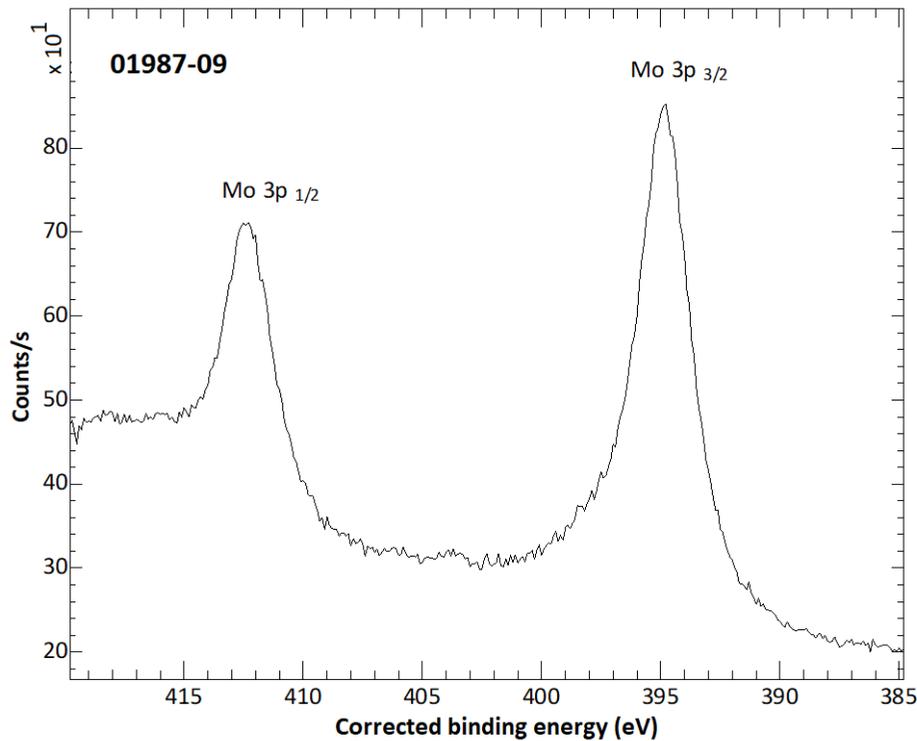


■ Accession #: 01987-07
 ■ Specimen: MoS₂
 ■ Technique: XPS
 ■ Spectral Region: Mo 2p_{1/2}
 Instrument: ULVAC-PHI Quantes
 Excitation Source: Cr K_α monochromatic
 Source Energy: 5414.8 eV
 Source Strength: 45 W
 Source Size: 100 × 100 μm²
 Analyzer Type: spherical sector
 Incident Angle: 22 °
 Emission Angle: 45 °
 Analyzer Pass Energy 112 eV
 Instrument Resolution: 1.17 eV
 Total Signal Accumulation Time: 4404 s
 Total Elapsed Time: 4854 s
 Number of Scans: 24

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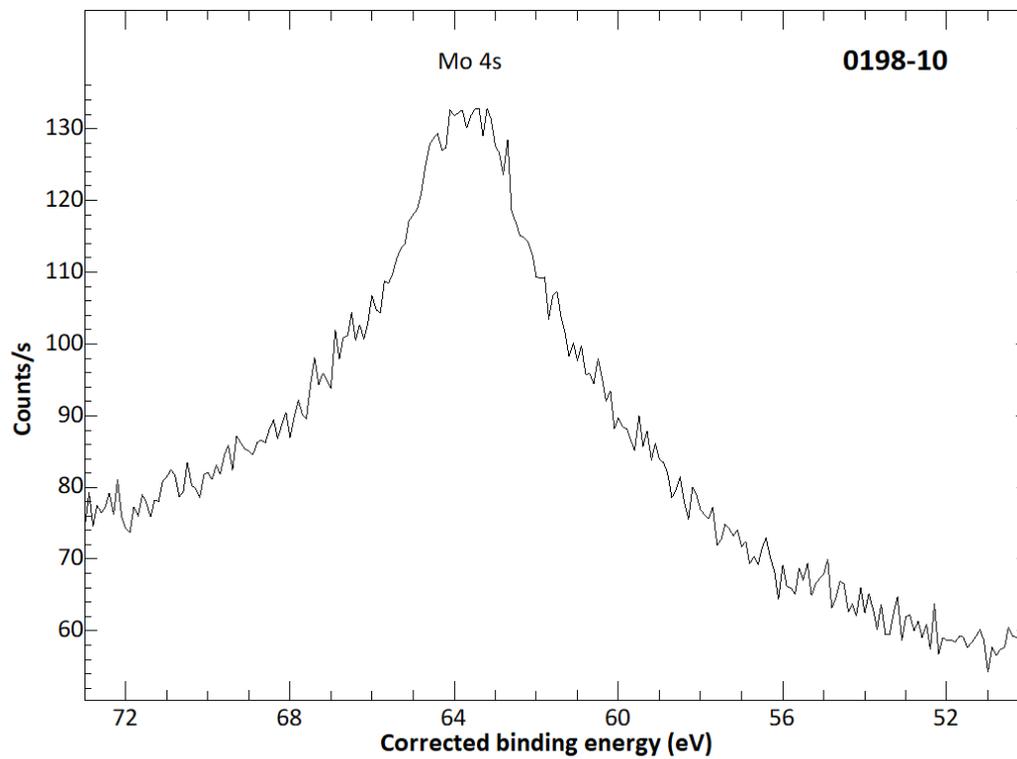


■ Accession #: 01987-08
 ■ Specimen: MoS₂
 ■ Technique: XPS
 ■ Spectral Region: Mo 3s
 Instrument: ULVAC-PHI Quantes
 Excitation Source: Cr K_α monochromatic
 Source Energy: 5414.8 eV
 Source Strength: 45 W
 Source Size: 100 × 100 μm²
 Analyzer Type: spherical sector
 Incident Angle: 22 °
 Emission Angle: 45 °
 Analyzer Pass Energy 112 eV
 Instrument Resolution: 1.17 eV
 Total Signal Accumulation Time: 6606 s
 Total Elapsed Time: 7278 s
 Number of Scans: 48

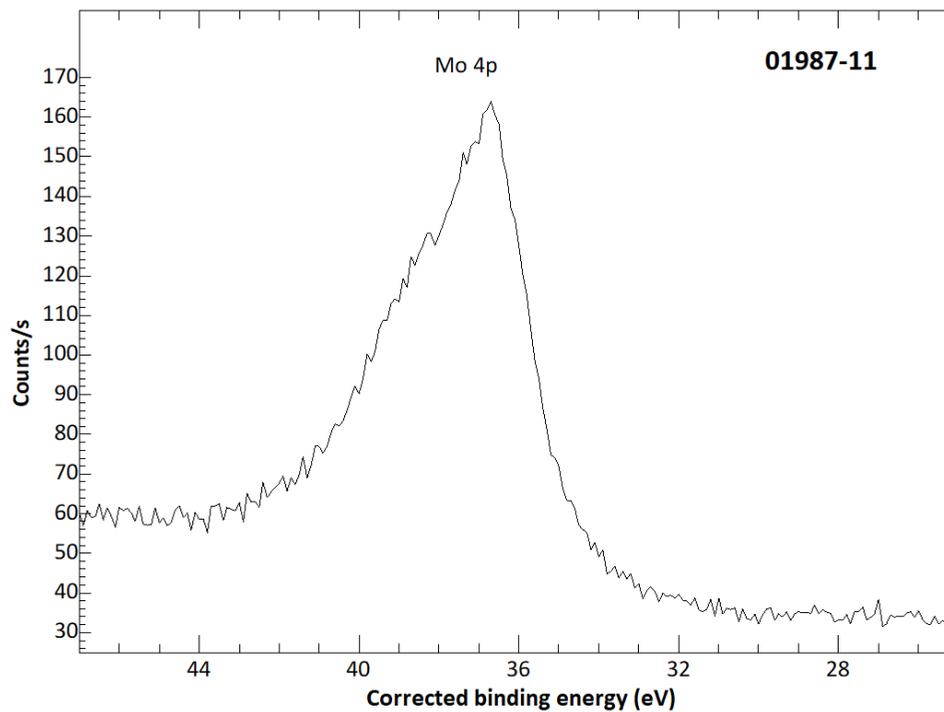


■ Accession #: 01987-09
 ■ Specimen: MoS₂
 ■ Technique: XPS
 ■ Spectral Region: Mo 3p
 Instrument: ULVAC-PHI Quantes
 Excitation Source: Cr K_α monochromatic
 Source Energy: 5414.8 eV
 Source Strength: 45 W
 Source Size: 100 × 100 μm²
 Analyzer Type: spherical sector
 Incident Angle: 22 °
 Emission Angle: 45 °
 Analyzer Pass Energy 112 eV
 Instrument Resolution: 1.17 eV
 Total Signal Accumulation Time: 6828 s
 Total Elapsed Time: 7518 s
 Number of Scans: 36

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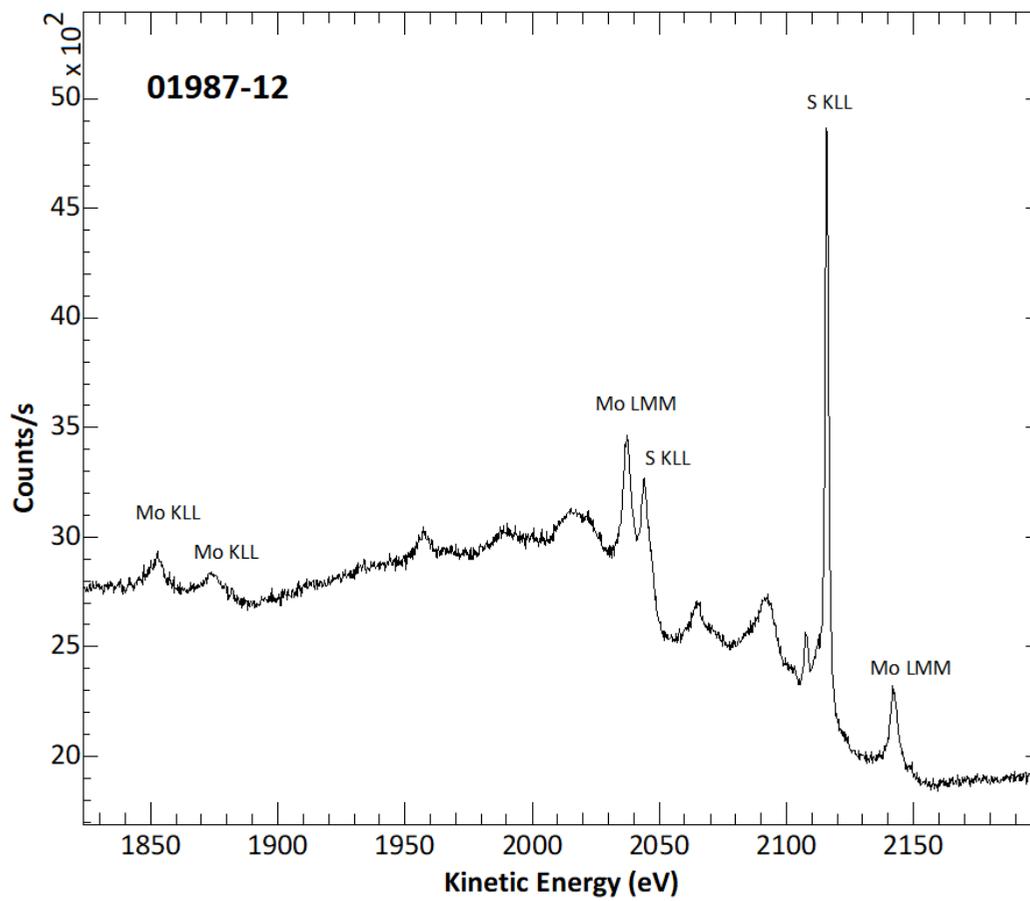


■ Accession #: 01987-10
 ■ Specimen: MoS₂
 ■ Technique: XPS
 ■ Spectral Region: Mo 4s
 Instrument: ULVAC-PHI Quantes
 Excitation Source: Cr K_α monochromatic
 Source Energy: 5414.8 eV
 Source Strength: 45 W
 Source Size: 100 × 100 μm²
 Analyzer Type: spherical sector
 Incident Angle: 22 °
 Emission Angle: 45 °
 Analyzer Pass Energy 112 eV
 Instrument Resolution: 1.17 eV
 Total Signal Accumulation Time: 10194 s
 Total Elapsed Time: 11238 s
 Number of Scans: 72



■ Accession #: 01987-11
 ■ Specimen: MoS₂
 ■ Technique: XPS
 ■ Spectral Region: Mo 4p
 Instrument: ULVAC-PHI Quantes
 Excitation Source: Cr K_α monochromatic
 Source Energy: 5414.8 eV
 Source Strength: 45 W
 Source Size: 100 × 100 μm²
 Analyzer Type: spherical sector
 Incident Angle: 22 °
 Emission Angle: 45 °
 Analyzer Pass Energy 112 eV
 Instrument Resolution: 1.17 eV
 Total Signal Accumulation Time: 6606 s
 Total Elapsed Time: 7278 s
 Number of Scans: 48

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■ **Accession #:** 01987-12
 ■ **Specimen:** MoS₂
 ■ **Technique:** XAES
 ■ **Spectral Region:** Mo KLL, Mo LMM, S KLL, Mo LMM
 Instrument: ULVAC-PHI Quantes
 Excitation Source: Cr K_α monochromatic
 Source Energy: 5414.8 eV
 Source Strength: 45 W
 Source Size: 100 × 100 μm²
 Analyzer Type: spherical sector
 Incident Angle: 22 °
 Emission Angle: 45 °
 Analyzer Pass Energy 140 eV
 Instrument Resolution: 1.17 eV
 Total Signal Accumulation Time: 23094 s
 Total Elapsed Time: 25410 s
 Number of Scans: 28