

CF₃(CF₂)₇(CH₂)₂SH Self-Assembled on Au and Subsequent Degradation Under the Influence of Ionizing Radiation as Measured by XPS

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X-ray photoelectron spectra are shown for a semifluorinated self-assembled monolayer based on 1H,1H,2H,2H-perfluorodecanethiol [CF₃(CF₂)₇(CH₂)₂SH] absorbed on a polycrystalline gold substrate. The effect of x-ray irradiation on the defluorination of the film, studied by following the time dependent variation in the C 1s spectral region, is also shown. This information has been used to elucidate the mechanism and kinetics of the elementary reaction steps that comprise defluorination. © 2000 American Vacuum Society.

Keywords: x-ray degradation; semifluorinated self-assembled monolayer

PACS: 79.60Dp, 79.60.Fr, 82.50.Gw

§ ◆ 007004sss

SPECIMEN DESCRIPTION

Host Material: Fluorinated self-assembled monolayer

Host Material Characteristics: homogeneous; solid; organic compound; thin film; coating

Chemical Name: 1H,1H,2H,2H-perfluorodecanethiol

Source: Au foil was sputtered with 2 keV electron until clean (by AES), immersed in 5 mmol 1H,1H,2H,2H-perfluorodecanethiol in ethanol for 12–24 h, and finally washed with ethanol hexanes and water.

Host Composition: CF₃(CF₂)₇(CH₂)₂SH

Form: monolayer

History & Significance: A semifluorinated self-assembled monolayer was prepared on an Au substrate and subsequently degraded under the influence of x-ray irradiation. The objective of this study was to understand the dynamics (mechanism and kinetics) of defluorination using a well-defined organic thin film as an initial reference.

As Received Condition: see entry for Specimen Manufacturer/Supplier

Analyzed Region: semifluorinated self-assembled monolayer on gold

Ex Situ Preparation/Mounting: Prepared as described in entry for Specimen Manufacturer/Supplier, then mounted on the PHI sample stub.

In Situ Preparation: none

Pre-Analysis Beam Exposure: ~5 min x-ray exposure for aligning the sample prior to spectra measurements

Charge Control: sample held at ground

Temp. During Analysis: 398 K

Pressure During Analysis: <6.65×10⁻⁵ Pa

INSTRUMENT DESCRIPTION

Manufacturer and Model: Perkin Elmer PHI 5400, Omnifocus 1A lens

Analyzer Type: spherical sector

Detector: position sensitive detector

Number of Detector Elements: 64

INSTRUMENT PARAMETERS COMMON TO ALL SPECTRA

■ Spectrometer

Analyzer Mode: constant pass energy

Throughput ($T=E^N$): $N=-1$

Excitation Source Window: 2 μm Al window

Excitation Source: Mg K_α

Source Energy: 1253.6 eV

Source Strength: 300 W

Source Beam Size: <25000

Analyzer Width: 3000 μm × 10000 μm

Signal Mode: multichannel direct

■ Geometry

Incident Angle: 9°

Source to Analyzer Angle: 53.8°

Emission Angle: 45°

Specimen Azimuthal Angle: 0°

Acceptance Angle from Analyzer Axis: 0°

Analyzer Angular Acceptance Width: 6° × 6°

■ Ion Gun

Manufacturer and Model: PHI 04-303

Energy: 4000 eV

Current: 25 mA

Current Measurement Method: Faraday cup

Sputtering Species: Ar

Spot Size (unrastered): 200 μm

Raster Size: 10000 μm × 10000 μm

Incident Angle: 40°

Polar Angle: 45°

Accession # 00616

Technique: XPS

Host Material: Fluorinated self-assembled monolayer

Instrument: Perkin Elmer PHI 5400, Omnifocus 1A lens

Major Elements in Spectrum: Au, C, F

Minor Elements in Spectrum: S

Printed Spectra: 9

Spectra in Electronic Record: 11

Spectral Category: comparison

Original Submission: 10/30/2000

Accepted for Publication: 11/28/2000

Azimuthal Angle: 111°

DATA ANALYSIS METHOD

Energy Scale Correction: All spectra are corrected using the Au $4f_{7/2}$ peak, with a known position of 83.80 eV.

Peak Shape and Background Method: Background correction was done using a Shirley function. All fits were performed using Gaussian spectral line shapes.

Quantitation Method: Quantitation was calculated using peak areas of the elements divided by their respective sensitivity factors (PHI Omnifocus 1A, at 54° source to analyzer angle).

ACKNOWLEDGMENTS

NSF Career Grant No. 9985372, and NSF, MRSEC (Johns Hopkins University).

REFERENCES

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SPECTRAL FEATURES TABLE

Spectrum ID #	Element/Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (counts)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
00616-03	C 1s	292.75	CF ₃
00616-03	C 1s	290.50	CF ₂
00616-03	C 1s	284.50	CH ₂ /C-C
00616-06	C 1s	292.79	CF ₃
00616-06	C 1s	290.50	CF ₂
00616-06	C 1s	284.50	CH ₂ /C-C
00616-07	C 1s	292.66	CF ₃
00616-07	C 1s	290.51	CF ₂
00616-07	C 1s	287.80	CF
00616-07	C 1s	284.96	CH ₂ /C-C
00616-08	C 1s	290.11	CF ₂
00616-08	C 1s	287.31	CF
00616-08	C 1s	284.56	CH ₂ /C-C
00616-09	C 1s	289.74	CF ₂
00616-09	C 1s	286.91	CF
00616-09	C 1s	284.47	CH ₂ /C-C
00616-01	Au 4d _{5/2}	334.6	2.388	24.4	...
00616-01 ^a	C 1s	290.5	0.296	24.8	...
00616-01	F 1s	687.7	1.00	49.0	...
00616-01	S 2p	161.8	0.666	1.7	...

^a Position of CF₂

ANALYZER CALIBRATION TABLE

Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (counts)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
00616-01	Au $4f_{7/2}$	83.75	85.5	...
00616-02	Au $4f_{7/2}$	83.80	1.29	49406	3.536	100	...
00616-03	Cu $2p_{3/2}$	933.0	14.5	...

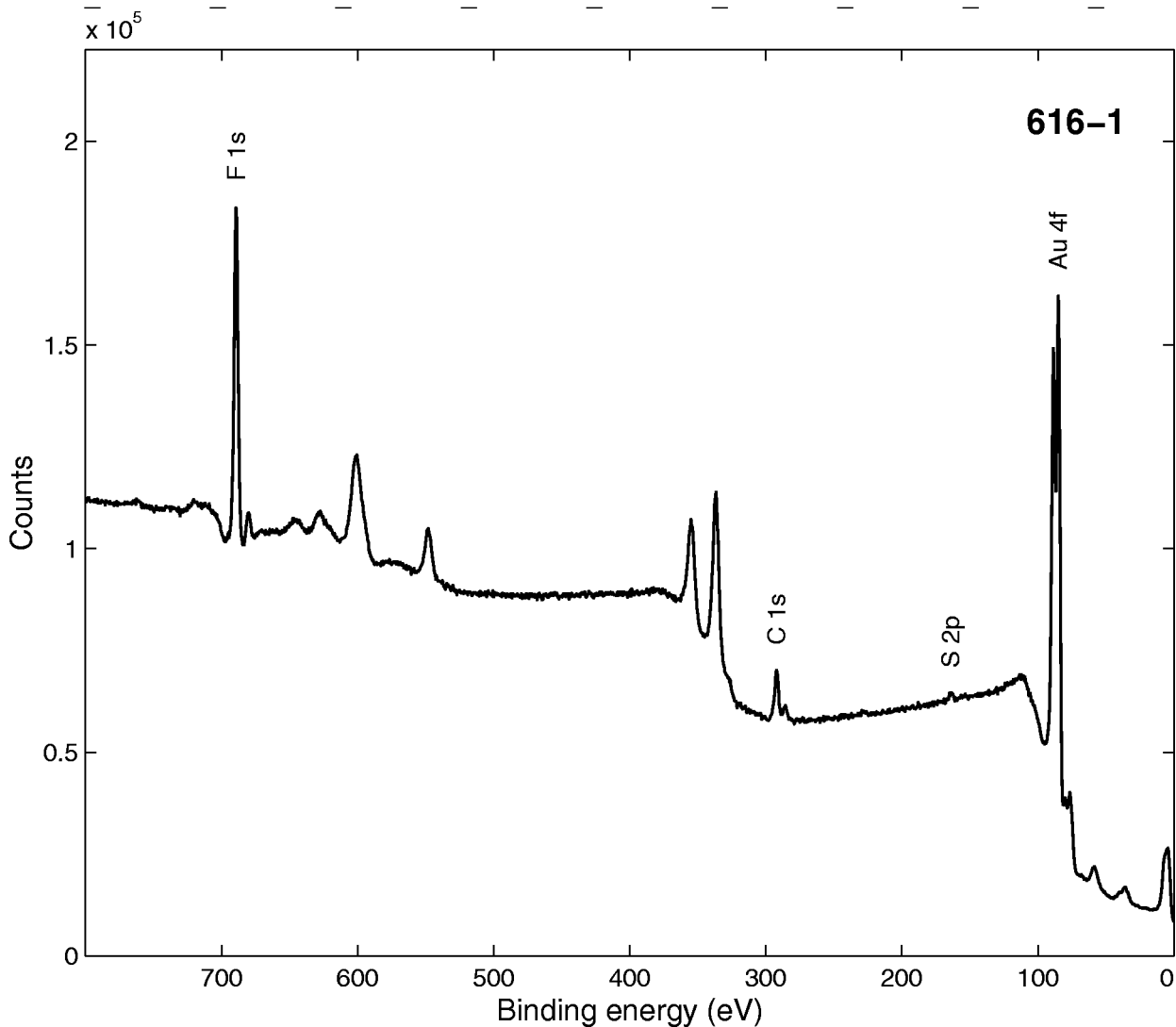
GUIDE TO FIGURES

Spectrum (Accession) #	Spectral Region	Sample Voltage*	Multiplier	Baseline	Comment #
616-1	Survey	0	1	0	1, 3
616-2	Au $4f$	0	1	0	1, 3
616-3	C $1s$	0	1	0	1, 3
616-4	F $1s$	0	1	0	1, 3
616-5	S $2p$	0	1	0	1, 3
616-6	C $1s$	0	1	0	1, 4
616-7	C $1s$	0	1	7000	1, 5
616-8	C $1s$	0	1	10000	1, 6
616-9	C $1s$	0	1	12000	1, 7
616-10 [NP]**	Survey	0	1	0	2, 3
616-11 [NP]	Au and Cu survey	0	1	0	1, 3, 8

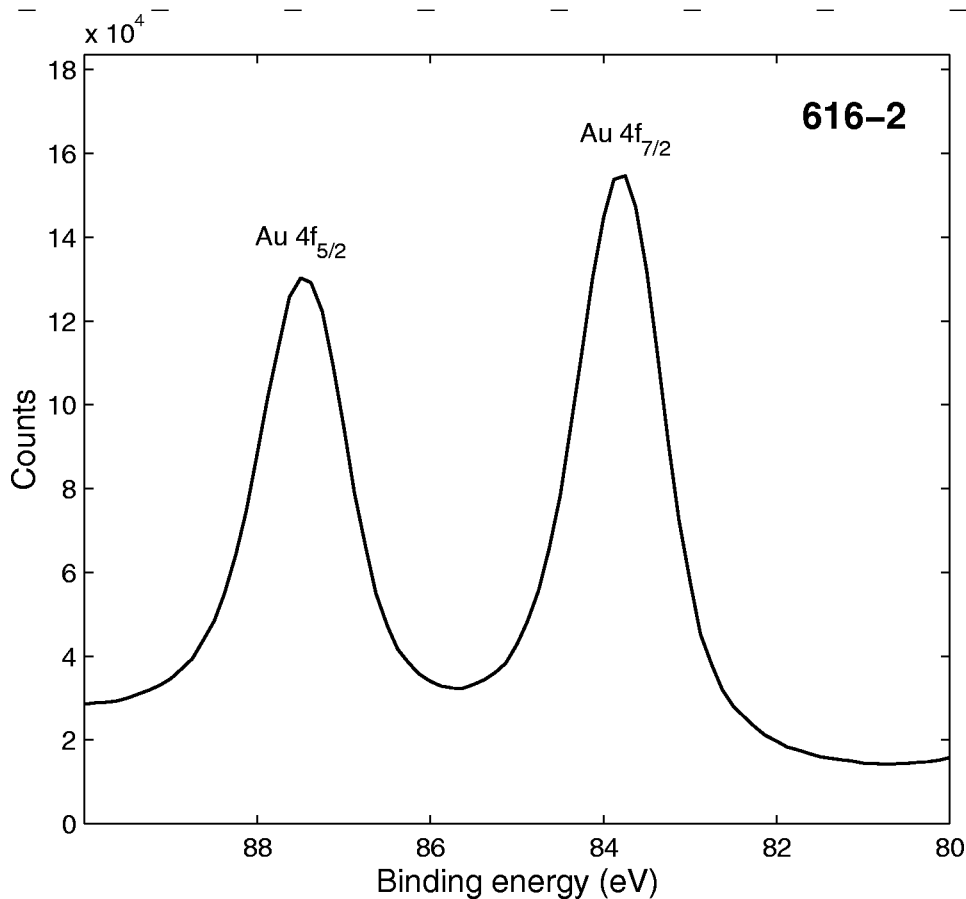
* Inferred sample potential relative to spectrometer ground due to charging, flood gun, or other phenomena.

** [NP] signifies not published; digital spectra are archived in SSS database but not reproduced in the printed journal.

1. Mg K_{α} excitation source
2. Al K_{α} excitation source
3. Initial scan
4. X-ray exposure time 15 min
5. X-ray exposure time 104 min
6. X-ray exposure time 331 min
7. X-ray exposure time 690 min
8. Calibration spectrum

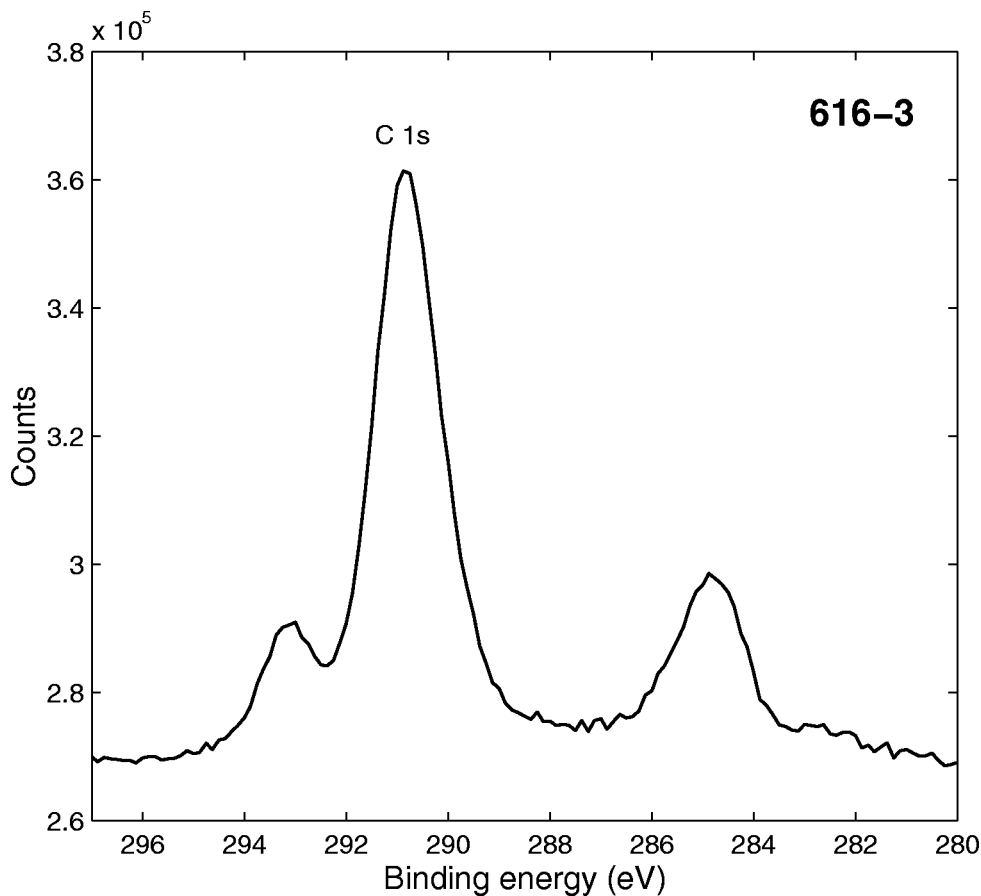


Accession #	00616-01
Host Material	Fluorinated self-assembled monolayer
Technique	XPS
Spectral Region	survey
Instrument	Perkin Elmer PHI 5400, Omnicfocus 1A lens
Excitation Source	Mg K_{α}
Source Energy	1253.6 eV
Source Strength	300 W
Source Size	<25 mm \times <25 mm
Analyzer Type	spherical sector
Incident Angle	9°
Emission Angle	45°
Analyzer Pass Energy	178.95 eV
Analyzer Resolution	2.68 eV
Total Signal Accumulation Time	160 s
Total Elapsed Time	190 s
Number of Scans	2
Effective Detector Width	2.68 eV



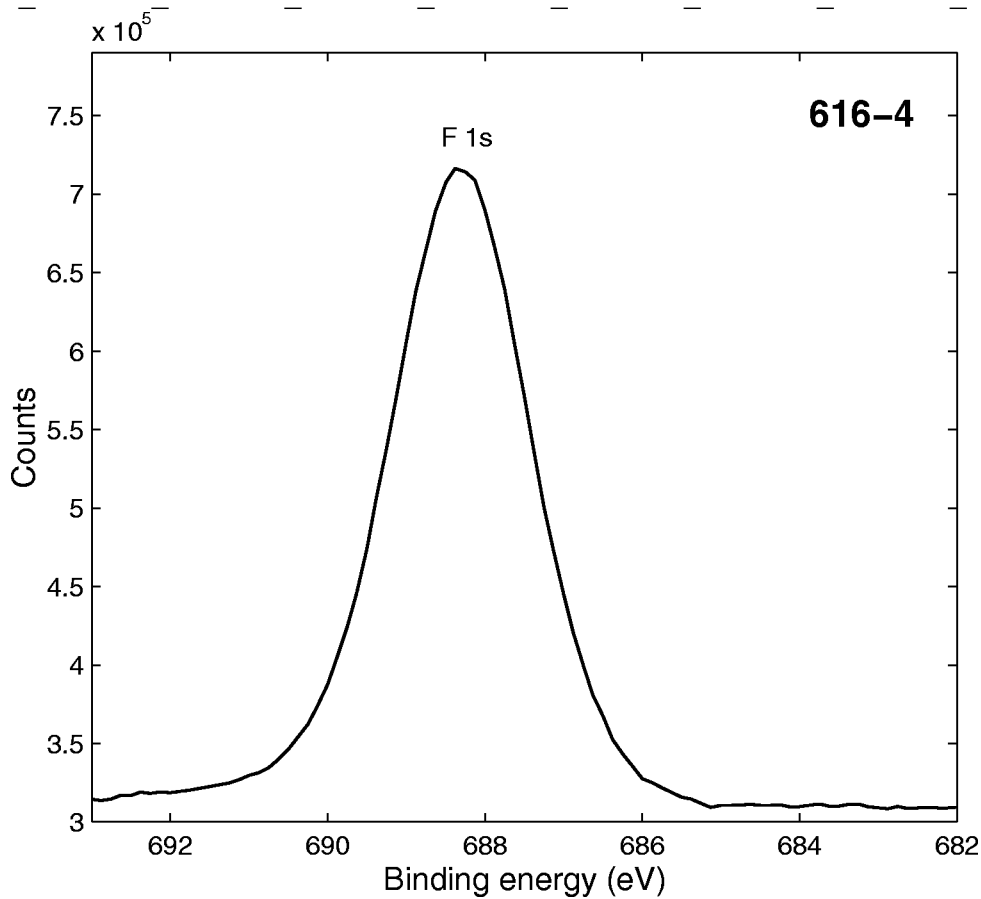
- **Accession #:** 00616-02
- **Host Material:** Fluorinated self-assembled monolayer
- **Technique:** XPS
- **Spectral Region:** Au 4f

Instrument: Perkin Elmer PHI 5400, Omnicfocus 1A lens
 Excitation Source: Mg K_{α}
 Source Energy: 1253.6 eV
 Source Strength: 300 W
 Source Size: <25 mm \times <25 mm
 Incident Angle: 9°
 Analyzer Type: spherical sector
 Analyzer Pass Energy: 44.75 eV
 Analyzer Resolution: 0.67 eV
 Emission Angle: 45°
 Total Signal Accumulation Time: 20 s
 Total Elapsed Time: 60 s
 Number of Scans: 5
 Effective Detector Width: 0.67 eV



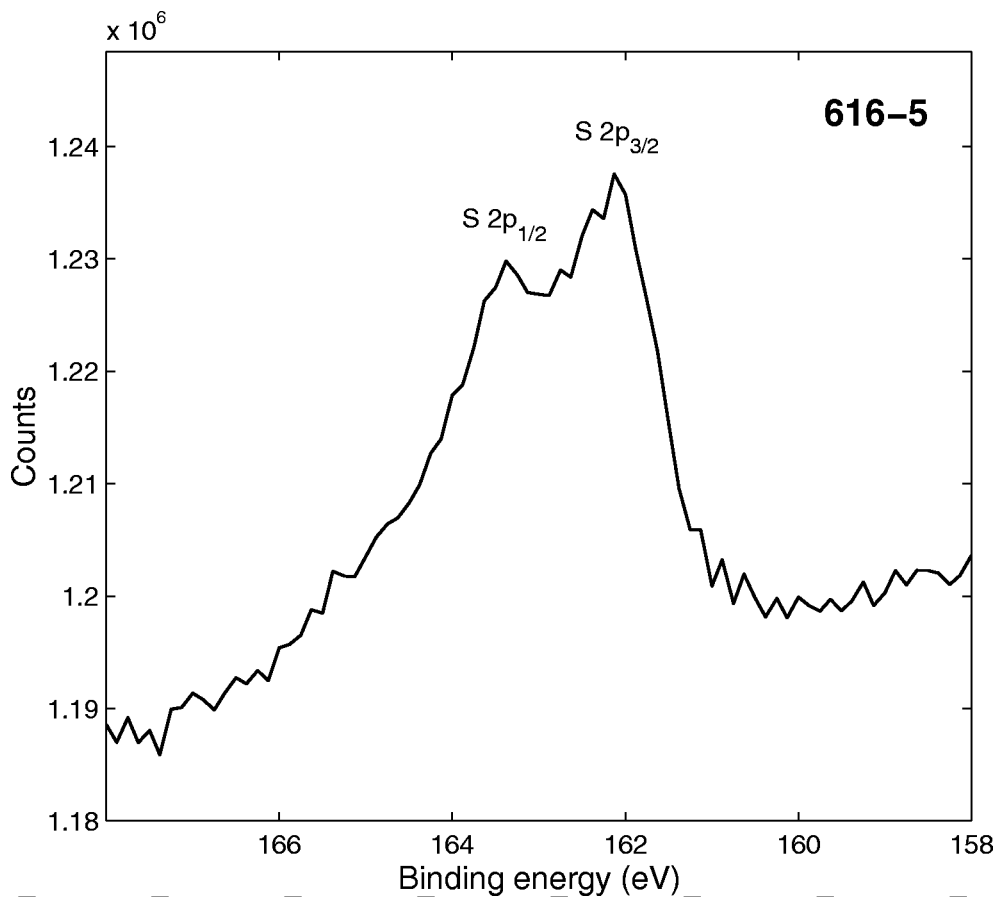
- **Accession #:** 00616-03
- **Host Material:** Fluorinated self-assembled monolayer
- **Technique:** XPS
- **Spectral Region:** C 1s

Instrument: Perkin Elmer PHI 5400, Omnicfocus 1A lens
 Excitation Source: Mg K_{α}
 Source Energy: 1253.6 eV
 Source Strength: 300 W
 Source Size: <25 mm \times <25 mm
 Incident Angle: 9°
 Analyzer Type: spherical sector
 Analyzer Pass Energy: 44.75 eV
 Analyzer Resolution: 0.67 eV
 Emission Angle: 45°
 Total Signal Accumulation Time: 380 s
 Total Elapsed Time: 510 s
 Number of Scans: 50
 Effective Detector Width: 0.67 eV
 Comment: 296.75 eV = CF₃,
 290.50 eV = CF₂,
 284.50 eV = C-C, CH₂



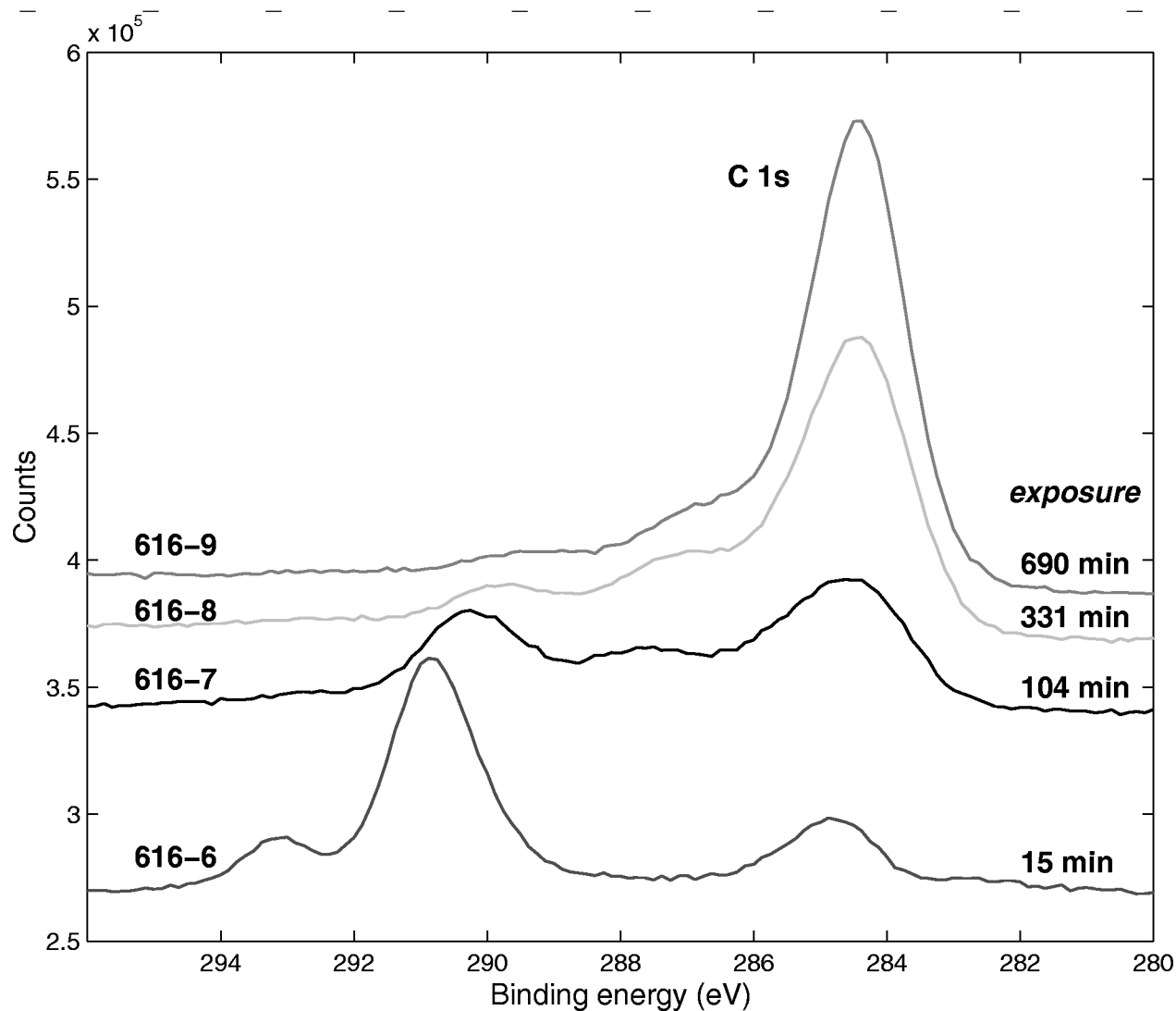
- **Accession #:** 00616-04
- **Host Material:** Fluorinated self-assembled monolayer
- **Technique:** XPS
- **Spectral Region:** F 1s

Instrument: Perkin Elmer PHI 5400, Omnifocus 1A lens
 Excitation Source: Mg K_{α}
 Source Energy: 1253.6 eV
 Source Strength: 300 W
 Source Size: <25 mm \times <25 mm
 Incident Angle: 9°
 Analyzer Type: spherical sector
 Analyzer Pass Energy: 44.75 eV
 Analyzer Resolution: 0.67 eV
 Emission Angle: 45°
 Total Signal Accumulation Time: 110 s
 Total Elapsed Time: 190 s
 Number of Scans: 25
 Effective Detector Width: 0.67 eV



- **Accession #:** 00616-05
- **Host Material:** Fluorinated self-assembled monolayer
- **Technique:** XPS
- **Spectral Region:** S 2p

Instrument: Perkin Elmer PHI 5400, Omnifocus 1A lens
 Excitation Source: Mg K_{α}
 Source Energy: 1253.6 eV
 Source Strength: 300 W
 Source Size: <25 mm \times <25 mm
 Incident Angle: 9°
 Analyzer Type: spherical sector
 Analyzer Pass Energy: 44.75 eV
 Analyzer Resolution: 0.67 eV
 Emission Angle: 45°
 Total Signal Accumulation Time: 800 s
 Total Elapsed Time: 1184 s
 Number of Scans: 200
 Effective Detector Width: 0.67 eV



Accession #	00616-06, 00616-07, 00616-08, 00616-09
Host Material	Fluorinated self-assembled monolayer
Technique	XPS
Spectral Region	C 1s
Instrument	Perkin Elmer PHI 5400, Omnifocus 1A lens
Excitation Source	Mg K _α
Source Energy	1253.6 eV
Source Strength	300 W
Source Size	<25 mm × <25 mm
Incident Angle	9°
Analyzer Type	spherical sector
Analyzer Pass Energy	44.75 eV
Analyzer Resolution	0.67 eV
Emission Angle	45°
Total Signal Accumulation Time	320 s
Total Elapsed Time	450 s
Number of Scans	50
Effective Detector Width	0.67 eV