

**Electronic Properties and Surface Electron Spectroscopies:  
XPS/UPS, Auger and ARPES**

**XPS: X-ray Photoelectron Spectroscopy**  
**UPS: Ultraviolet Photoelectron Spectroscopy**  
**AES: Auger Electron Spectroscopy**  
**ARPES: Angle-Resolved PhotoEmission Spectroscopy**

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## XPS und UPS



Kai Siegbahn  
1918-2007

Die Energie der Photoelektronen liegt im Bereich von 10-2000eV. Demnach kommen die Elektronen max aus einer Tiefe von einigen Monolagen. Werden Röntgenstrahlen zur Anregung benutzt so wird die Methode **X-ray photoelectron spectroscopy (XPS)** bezeichnet. XPS wurde zum ersten Mal von Kai Siegbahn (Uppsala) 1954 durchgeführt (1981 Nobelpreis). Hierzu wurde ein Energieanalysator entwickelt, der ein Auflösungsvermögen von  $\Delta E/E=10^5$  erreicht hat. Wurde auch ESCA (electron spectroscopy for chemical analysis) genannt. XPS ist heute aber gebräuchlicher, weil verschiedene andere elektronenspektroskopische Methoden zur chemischen Analyse benutzt werden (z.B. EELS). XPS wird vor allem für die Untersuchung der Rumpfelektronenzustände (core level spectroscopy) benutzt. Wird ultraviolette Strahlung eingestrahlt so wird von **Ultraviolet Photoelectron spectroscopy (UPS)** gesprochen. UPS wird zur Analyse der Valenzbänder benutzt und wird häufig zur Untersuchung des Bindungscharakters von adsorbierten Molekülen verwendet.

## Photonenquellen

Aus einem Filament werden Elektronen thermisch emittiert und auf eine Anode beschleunigt (typ. 20kV). Als Anode wird ein Material verwendet, das über einen kleinen Bremsstrahlungsuntergrund verfügt und eine schmale charakteristische Linienemission hat (möglichst eine dominierende Linie).

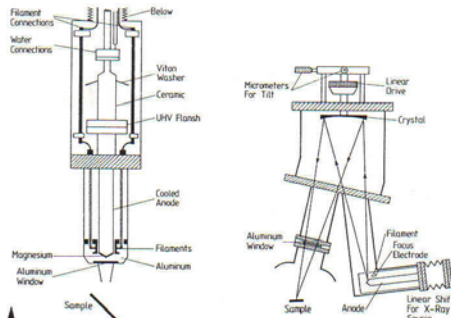


Fig. XI.3. Cross-sectional view of an X-ray source for X-ray Photoemission Spectroscopy (XPS). The anode, composed of either Mg or Al, is water cooled

Fig. XI.4. Schematic of an X-ray monochromator for high-resolution XPS. The X-ray source is flanged to an UHV chamber containing a crystal mirror which acts, by means of Bragg reflection, as a dispersive element

Speziell günstig haben sich Al(1486eV) und Mg(1253eV) erwiesen. Daneben wurden auch Na(1041eV), Si(1739eV) und Y(132,3eV) verwendet, wobei Y einen Spezialfall darstellt, der bereits im Übergangsbereich zu UPS liegt. Die Linienbreite ist im Bereich von 0.5-1.0eV, sodass Feinstrukturen wie chemische Shifts nur schwer beobachtbar sind. Die Verwendung eines Monochromators ist deshalb notwendig für die Untersuchung der Feinstruktur der „Core levels“

## UV-Lampe

Zur Erzeugung von UV-Licht werden Gas-Entladungslampen verwendet. Diese Lampen sind über differentiell gepumpte Kapillaren mit dem UHV-System verbunden. (gute UV-durchlässige Fenster sind nicht erhältlich). Als besonders günstig hat sich He erwiesen. Je nach Druck ist die He I Linie (1 Torr) bzw. die He-II-Linie (0.1 Torr) dominant. He I hat eine sehr intensive Linie bei 21.22eV. Linienbreite: 3-20meV, was die Untersuchung von Feinstrukturen, wie chemical shifts zulässt.

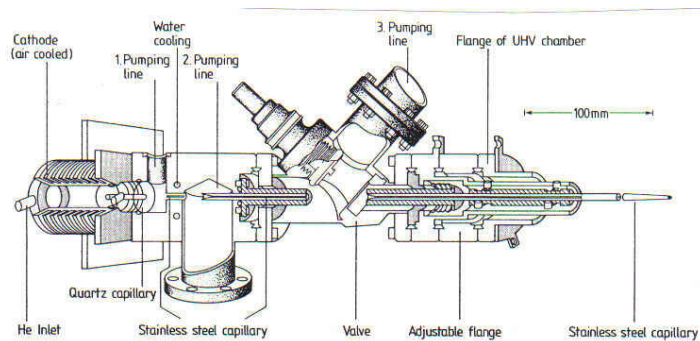
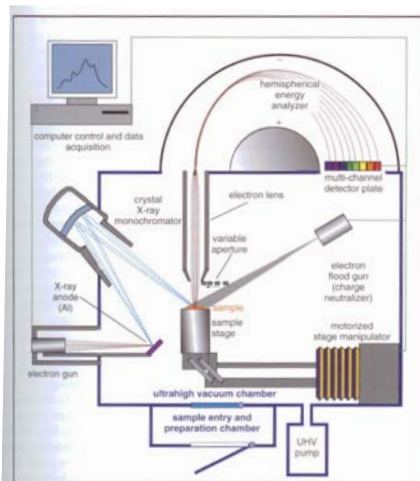


Fig. XI.2. Cross-sectional view of a UV discharge lamp for UV Photoemission Spectroscopy (UPS). The discharge quartz capillary is water cooled; three pump connections allow differential pumping; an UHV valve can interrupt the direct connection between discharge volume and UHV chamber

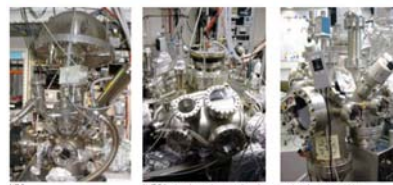
## Zusammenstellung von Photonquellen

Source	Energy [eV]	Relative intensity	Typical intensity at the sample [photons/s]	Linewidth [meV]
He I	21.22	100	$1 \cdot 10^{12}$	3
Satellites	23.09, 23.75, 24.05	< 2 each		
He II	40.82	20*	$2 \cdot 10^{11}$	17
	48.38	2*		
Satellites	51.0, 52.32, 53.00	< 1* each		
Ne I	16.85 and 16.67	100	$8 \cdot 10^{11}$	
Ne II	26.9	20*		
	27.8	10*		
	30.5	3*		
Satellites	34.8, 37.5, 38.0	< 2 each		
Ar I	11.83	100	$6 \cdot 10^{11}$	
	11.62	$80 \pm 40^*$		
Ar II	13.48	16*		
	13.30	10*		
YM <sub>1</sub>	132.3	100	$3 \cdot 10^{11}$	450
Mg K <sub>α1,2</sub>	1253.6	100	$1 \cdot 10^{12}$	680
Satellites K <sub>α3</sub>	1262.1	9		
	K <sub>α4</sub> 1263.7	5		
Al K <sub>α1,2</sub>	1486.6	100	$1 \cdot 10^{12}$	830
Satellites K <sub>α3</sub>	1496.3	7		
	K <sub>α4</sub> 1498.3	3		

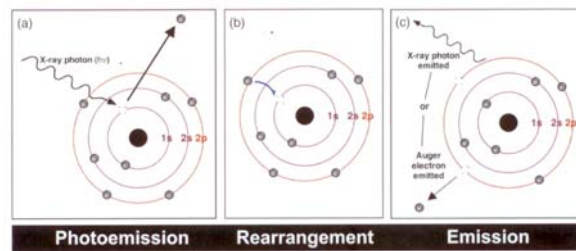
## Nanojunction-Lab at PSI



Instrument overview:



## XPS: Model



## Photoelectron Spectroscopy

Photonen werden eingestrahlt und absorbiert. Die emittierten Photoelektronen werden mittels eines Energieanalysators untersucht (Halbkugel oder 127°-Zylinderanalysator). Die kinetische Energie der Photoelektronen,  $E_{kin}$ , hängt von der Photonenergie  $h\nu$ , der Austrittsarbeit  $\phi$  und der Bindungsenergie  $E_b$  ab.

$$E_{kin} = h\nu - E_b - \phi$$

(Einsteinbeziehung, siehe Photoeffekt)

Damit ergibt das Spektrum der Photoelektronen ein Abbild der Bandstruktur. Als Nullpunkt wird üblicherweise die Fermi-Energie benutzt, welche bei Metallen den Photoelektronen mit höchster Energie entspricht. (Zur Kalibrierung bei Halbleitern und Isolatoren werden auch häufig „Metall-overlayer“ verwendet)

## XPS: Core Level Binding Energies

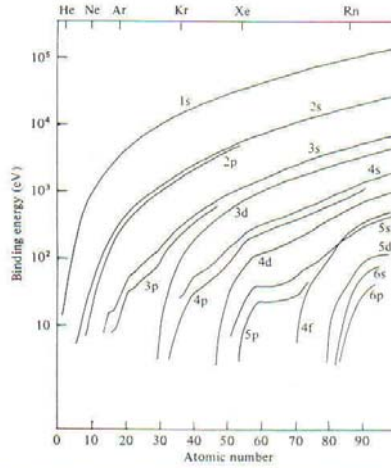


Fig. 3.15 Core electron binding energies of filled levels of the elements. Note that the majority of levels lie below about  $10^3$  eV and are therefore accessible to conventional laboratory source XPS (from Wertheim (1978) based on the tabulated values of Siegbahn *et al.*, 1967).

## XPS: Photoemission Cross-Section

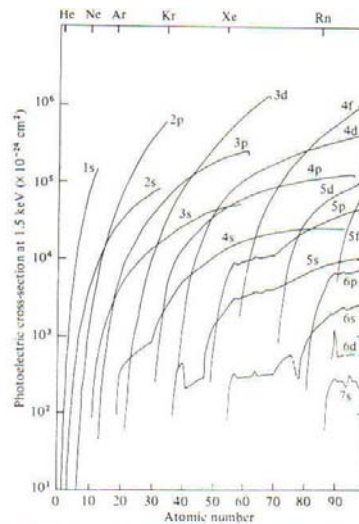


Fig. 3.16 Calculated cross-sections for photoemission from occupied levels of the elements for 1.5 keV photons (from Wertheim (1978) based on the calculated value of Scofield, 1976).

# Typisches XPS-Spektrum

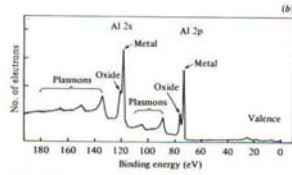
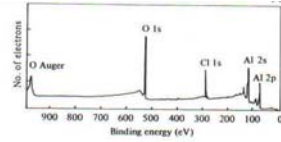
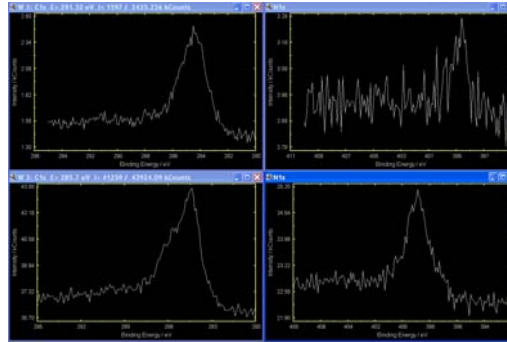
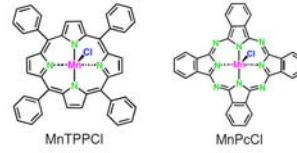
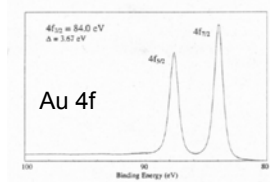
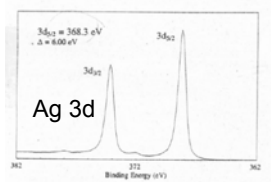
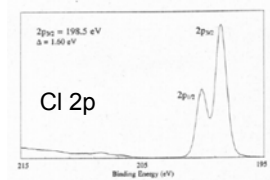
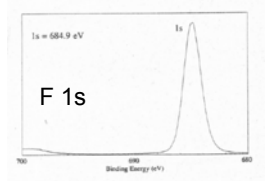
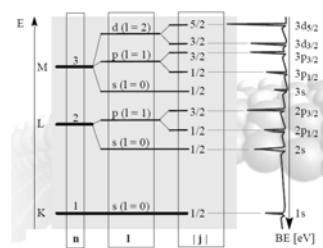
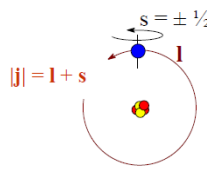
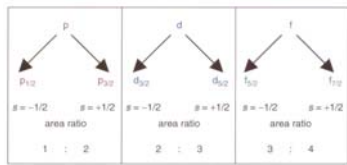
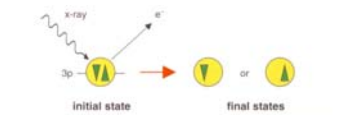


Fig. 3.11 Typical XPS spectra obtained from an oxidized and partly contaminated Al sample taken using monochromatic Al K<sub>α</sub> radiation. (a) shows the overall features with the main core level emissions labelled. (b) shows the low binding energy region on an expanded scale; plasmon loss structure and 'chemically shifted' Al emission lines are labelled (after Fadley, 1978).



# XPS: Spectral Features/ Spin-Orbit Coupling



# XPS: Chemical Shift

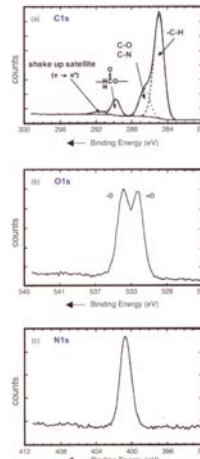
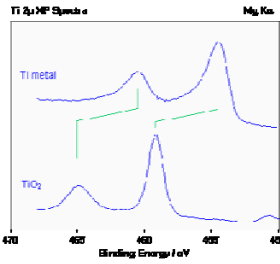
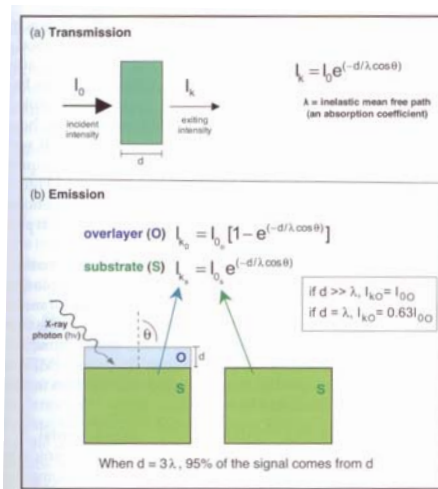


Figure 3.11 (a) The C<sub>1s</sub> spectrum (resolved into component peaks) for the hard-segment polyurethane; (b) the O<sub>1s</sub> spectrum for the hard-segment polyurethane; (c) the N<sub>1s</sub> spectrum for the hard-segment polyurethane

# XPS: Layer Thickness



## Self-Assembled Monolayers (SAMs)

$$I_s \propto e^{-d/\lambda_s} \quad I_c \propto (1 - e^{-d/\lambda_c})$$

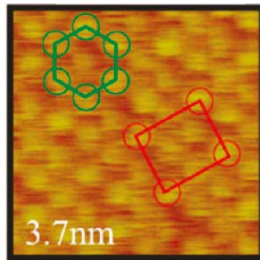
$$I_c / I_s = A [(1 - e^{-d/\lambda_c}) / e^{-d/\lambda_s}]$$

$$\lambda \text{ (\AA)} = 0.3 (E_{kin})^{0.64}$$

$$\text{DDT/Au} \approx 15 \text{ \AA} \text{ as reference}$$

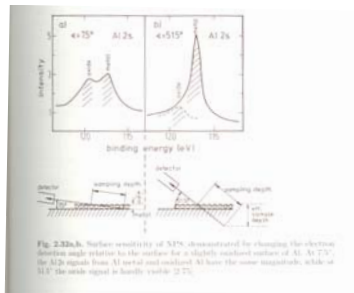
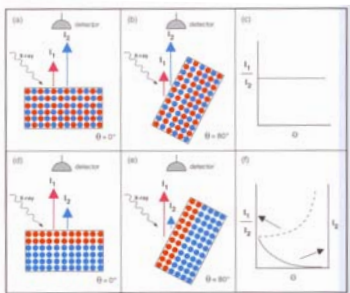
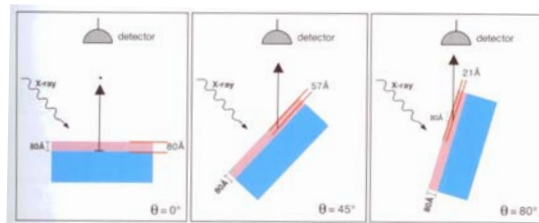
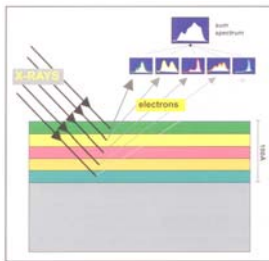
## XPS: Molecular Packing Density

Sample	Thickness	No. of Atoms	PD
Ref.	✓	✓	✓
Sample X	✓	✓	✓



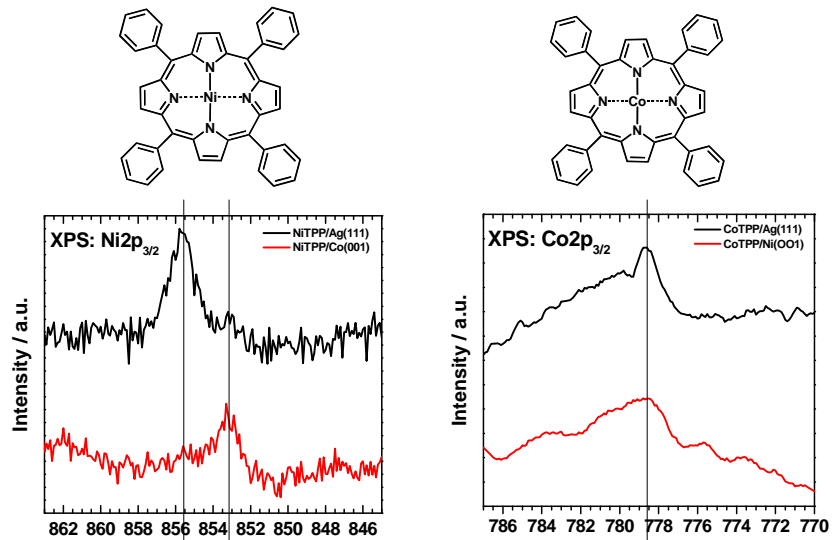
JPC C 2009, 113, 18312

## XPS: Depth Profiling

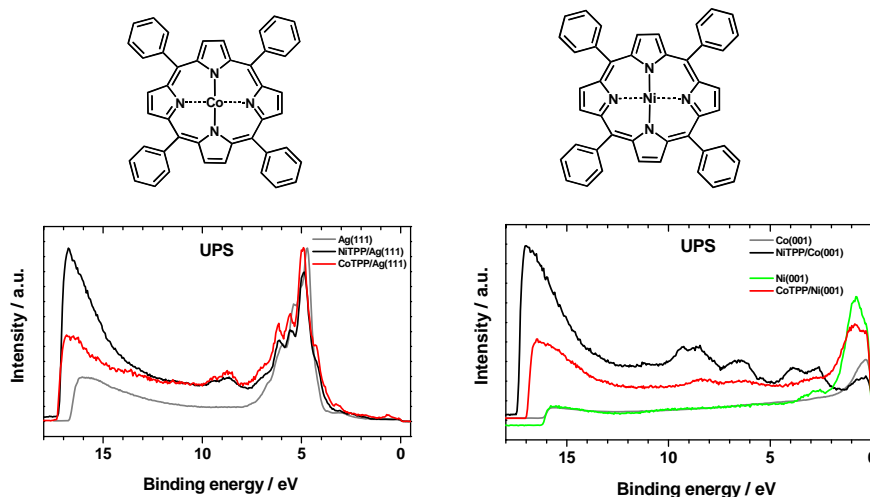




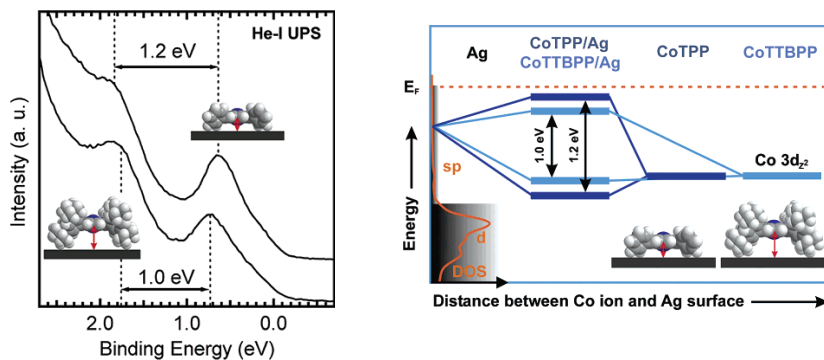
## XPS: Probing Electronic Interaction



## UPS: Probing $\phi$ and Electronic Interaction

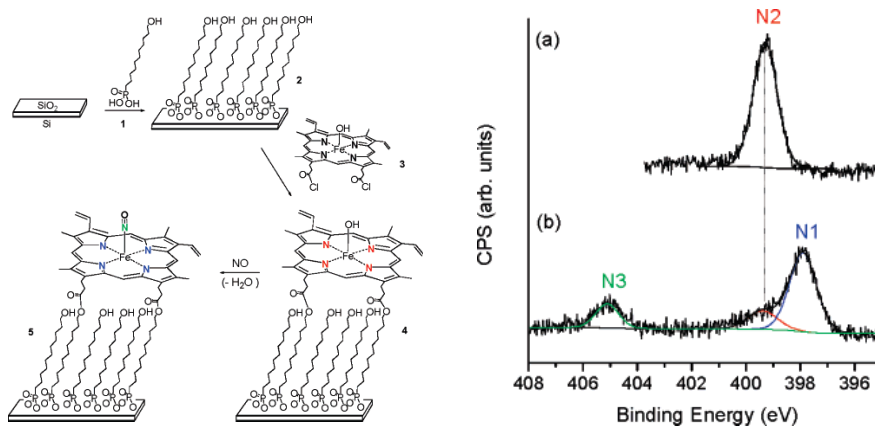


## UPS: Probing Electronic Interactions



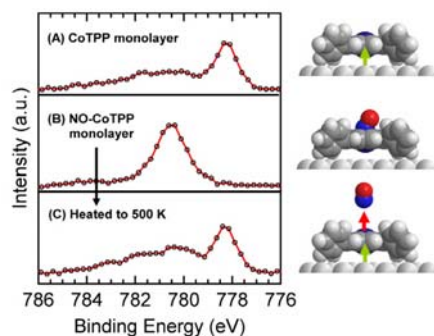
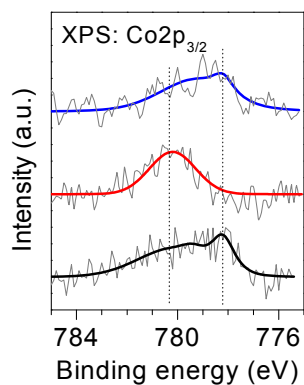
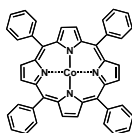
*J. Phys. Chem. C* 2007, 111, 3090

## XPS: Determination of Nitric Oxide



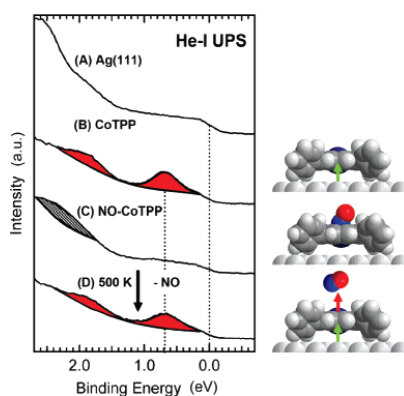
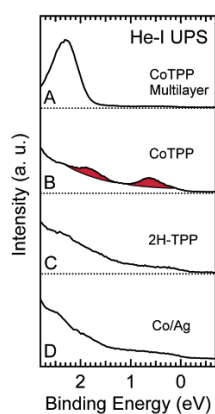
*J. Am. Chem. Soc.* 2007, 129, 6980

## XPS: Monitoring Electronic Interactions



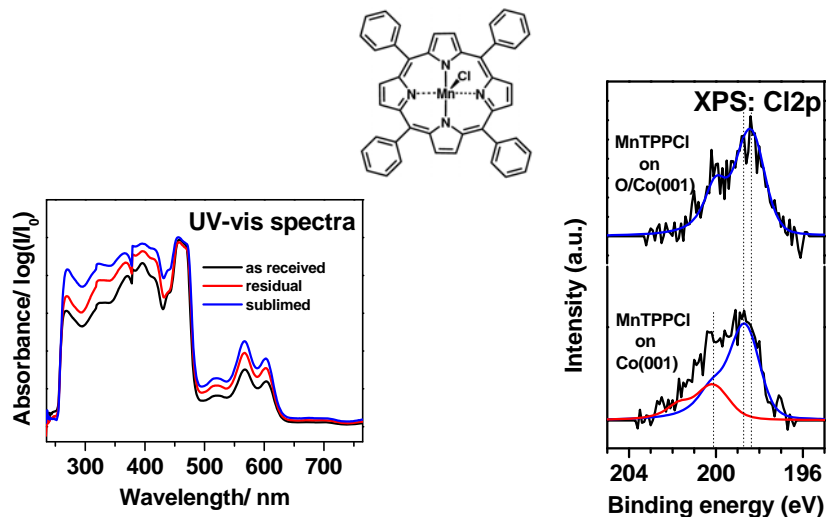
*J. Am. Chem. Soc.* 2007, 129, 12110

## UPS: Monitoring Electronic Interactions



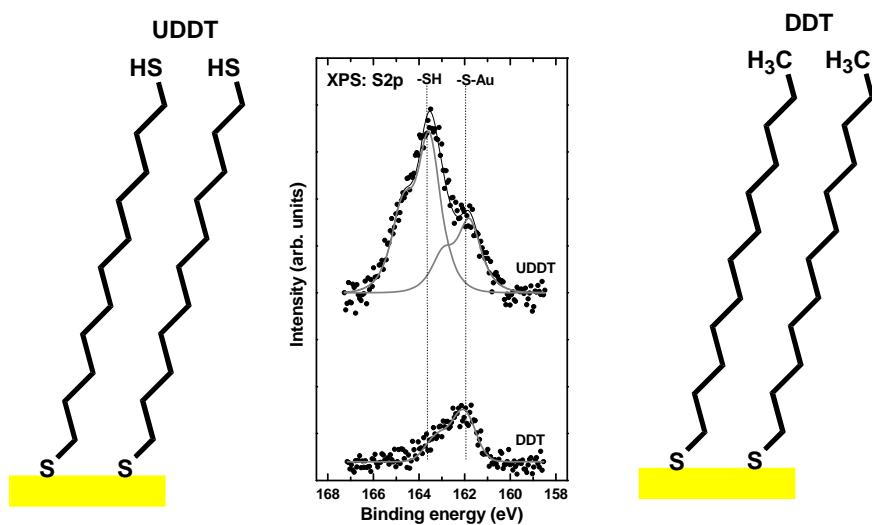
*J. Am. Chem. Soc.* 2007, 129, 12110

## XPS: Catalytic Reactions on Surface

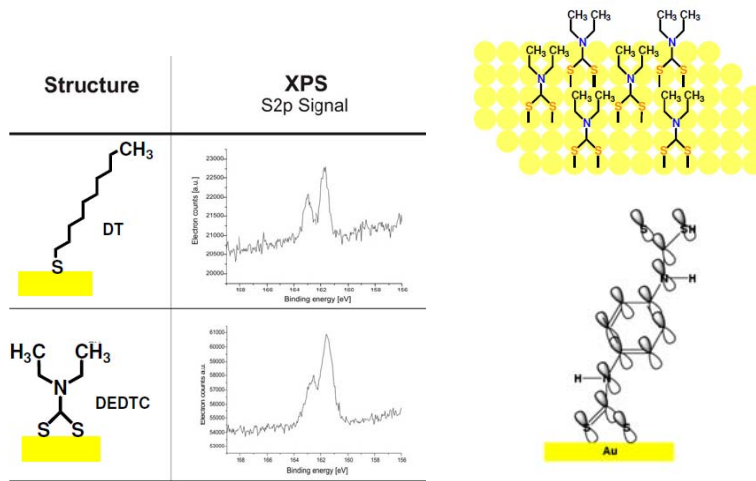


*J. Phys. Chem. Lett.* 2010 (in press)

## XPS: Self-Assembled Monolayers I

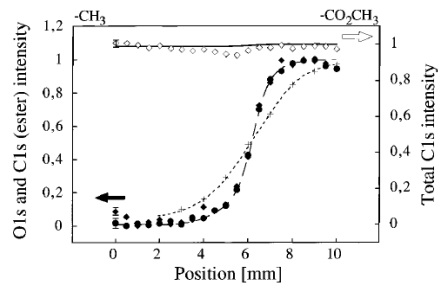
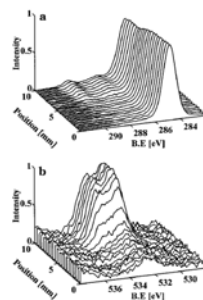
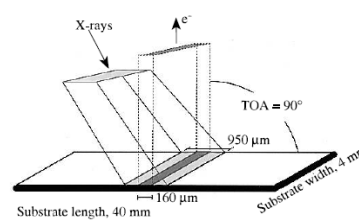
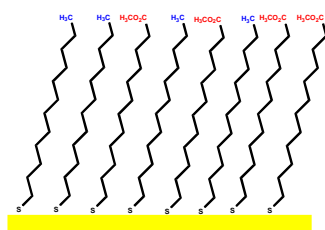


## XPS: Self-Assembled Monolayers II



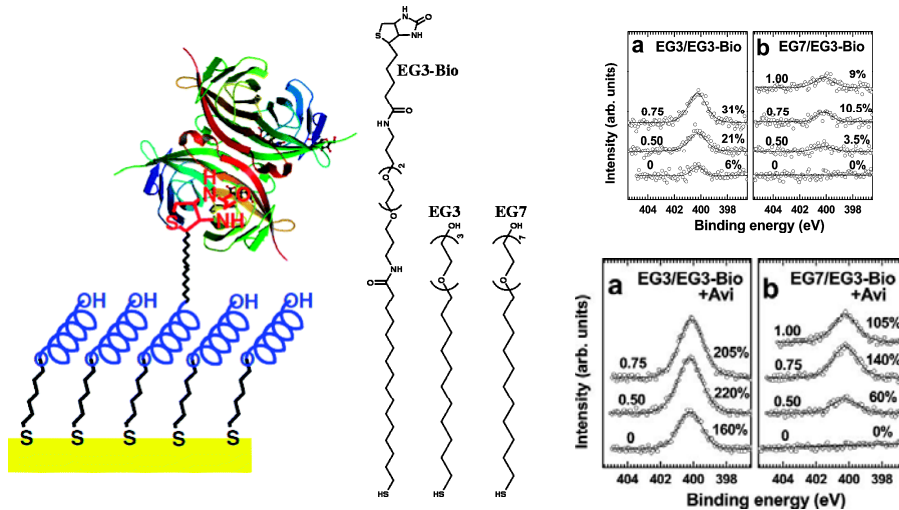
*J. Phys. Chem. Lett.* 2010, 1, 813

## XPS: Probing Molecular Gradients



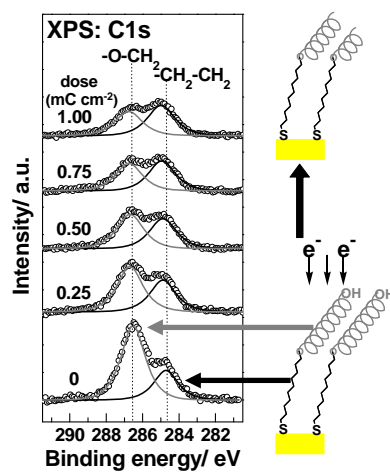
*Langmuir* 1997, 13, 5329

## XPS: Protein Adsorption Study



Langmuir 2009, 25, 9189

## XPS: Monitoring Electron-Irradiation on SAM



Angew. Chem. Int. Ed. 2009, 48, 5833

## XPS: Beam Damage/ Lithography

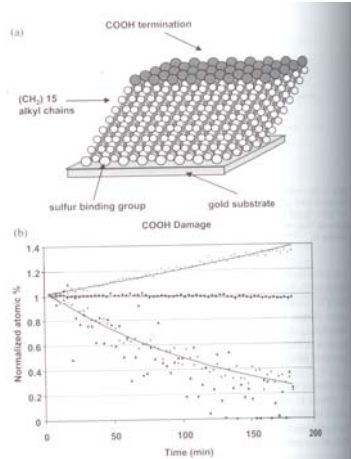


Figure 5. (a) illustration of a self-assembled monolayer formed on a Au substrate. Normalized atom ratios for a 15-carbon chain self-assembled monolayer terminated on COOH attached to a Au substrate observed as a function of time. Several XPS photoelectron peaks were measured: Au 4f peak [•], C 1s (C-H, C-C) [▲], C 1s (C=O) [●] and O 1s [×]. The most rapid and largest changes are a loss of the O in the COOH termination. The increase in the Au substrate signal is likely due to loss of H from the self-assembled monolayer as the  $(\text{CH}_2)_{15}$  hydrocarbon chain is damaged. The C 1s (made up of C-H and C-C bonded carbon) peak remains relatively constant, suggesting little loss of C from  $\text{CH}_2$  units in the hydrocarbon chain during the damage. Trend lines are shown for the full C 1s (C-H, C-C) and O 1s. Because the data for the smaller C 1s (C=O) peak is somewhat noisy no trend line is shown. The data is generally consistent with the O 1s data.

## XPS: Imaging

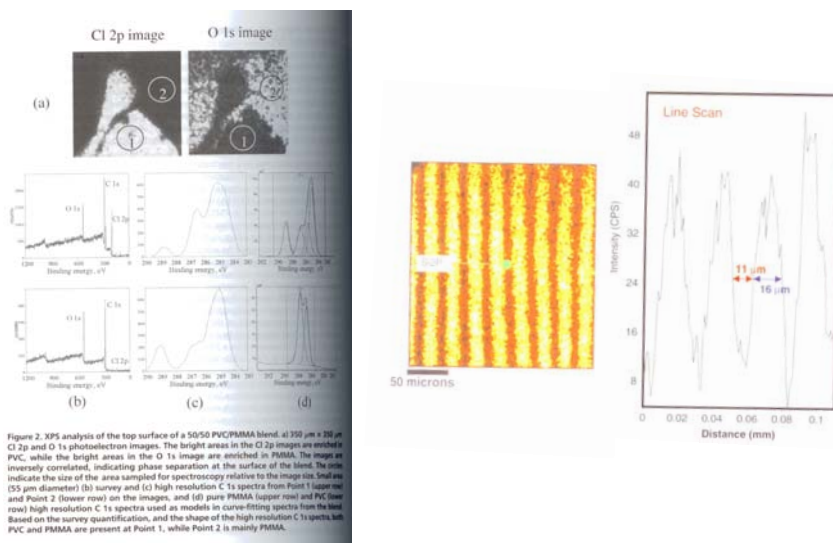


Figure 2. XPS analysis of the top surface of a 50/50 PVC/PMMA blend. (a)  $350 \mu\text{m} \times 350 \mu\text{m}$  Cl 2p and O 1s photoelectron images. The bright areas in the Cl 2p image are enriched PVC, while the bright areas in the O 1s image are enriched in PMMA. The images are inversely correlated, indicating phase separation at the surface of the blend. The size indicates the size of the area sampled for spectroscopy relative to the image size. Small size (50  $\mu\text{m}$  diameter) (b) survey and (c) high resolution C 1s spectra from Point 1 (upper row) and Point 2 (lower row) on the images. and (d) pure PMMA (upper row) and PVC (lower row) high resolution C 1s spectra used as models in curve-fitting spectra from the blend. Based on the survey quantification, and the shape of the high resolution C 1s spectra, both PVC and PMMA are present at Point 1, while Point 2 is mainly PMMA.

# Auger Electron Spectroscopy (AES)

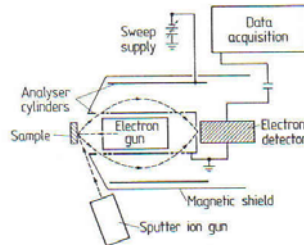


Fig. III.3. Schematic plot of a standard experimental set-up for Auger Electron Spectroscopy (AES). The primary electron beam is generated by an electron gun which is integrated on the central axis of a Cylindrical Mirror Analyser (CMA). An additional sputter ion gun provides the possibility of depth analysis

Das Primärelektron wechselwirkt mit der Oberfläche und erzeugt ein Augerelektron, welches ein Abbild der Rumpfelektronenbindungsenergien ist. Es handelt sich um eine Rumpfelektronenspektroskopie. (core level spectroscopy).

Elektronenkanone: 2000-5000eV

CMA-Energieanalysator, Retarding field analysator oder Halbkugelanalysator

Bei gewissen CMA-Analysatoren ist e-Kanone integriert, was für Tiefenprofilanalyse von Vorteil ist (Kombination mit „ion sputtering“)

# Auger-prozess

Der Augerprozess wird in 3 Etappen eingeteilt:

- 1) Das Primärelektron erzeugt ein Loch in einem Rumpfelektronenzustand (K oder L-Schale) mittels Ionisation.
- 2) Das Loch wird durch ein Elektron aus einer höheren Schale aufgefüllt (filling process).
- 3) Die Energie welche in 2 gewonnen wurde, wird auf Elektron der gleichen oder einer verschiedenen Schale übertragen, welches dann ausgesandt wird. Das Augerelektron hat eine charakteristische Energie, was zur Elementanalyse verwendet wird.

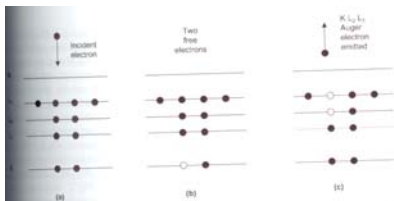


Figure 1. Illustration of the  $K_{L_2L_3}$  Auger process: (a) atom showing electrons present in the K and L levels before an electron is removed from the K level, (b) after removal of an electron from the K level and (c) following the Auger process where a  $K_{L_2L_3}$  Auger electron is emitted. In (c) one L level electron fills the K vacancy and the other L level electron is ejected due to the energy available on filling the K level.

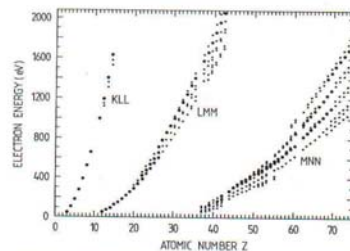


Fig. III.2. Principal Auger electron energies as a function of the atomic number Z. The strongest transitions of each element are indicated by bold points [III.2]



## Typisches AES-Spectra

