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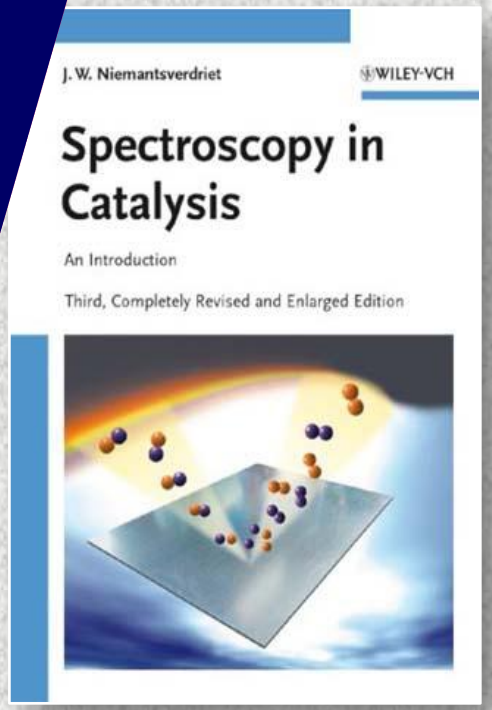
Characterization of solid catalysts

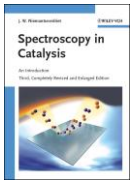
3. XPS



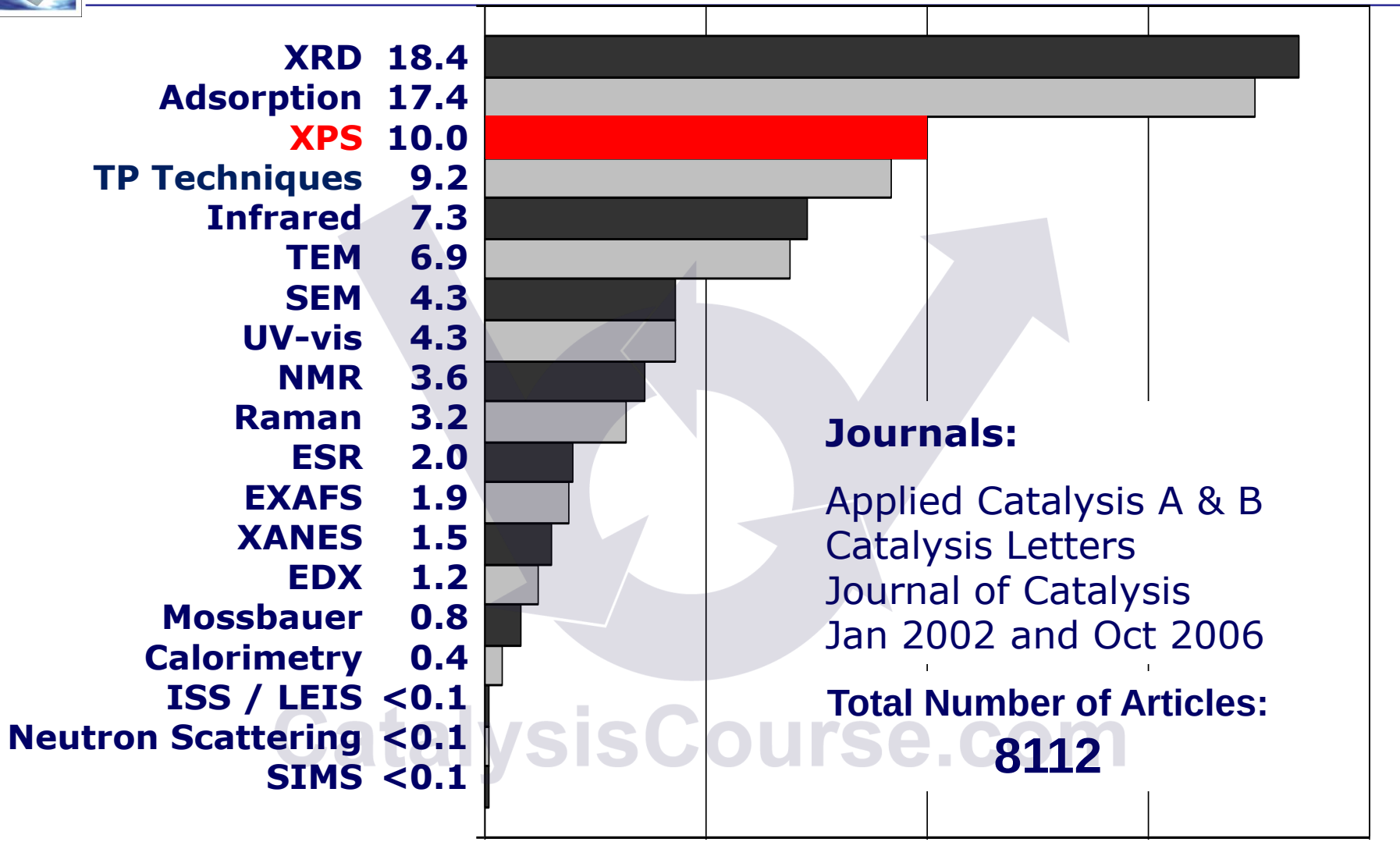
Prof dr J W (Hans) Niemantsverdriet
Schuit Institute of Catalysis

TU/e Technische Universiteit Eindhoven University of Technology

Where innovation starts



How often are techniques used



Journals:

Applied Catalysis A & B
Catalysis Letters
Journal of Catalysis
Jan 2002 and Oct 2006

Total Number of Articles:

8112

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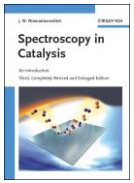
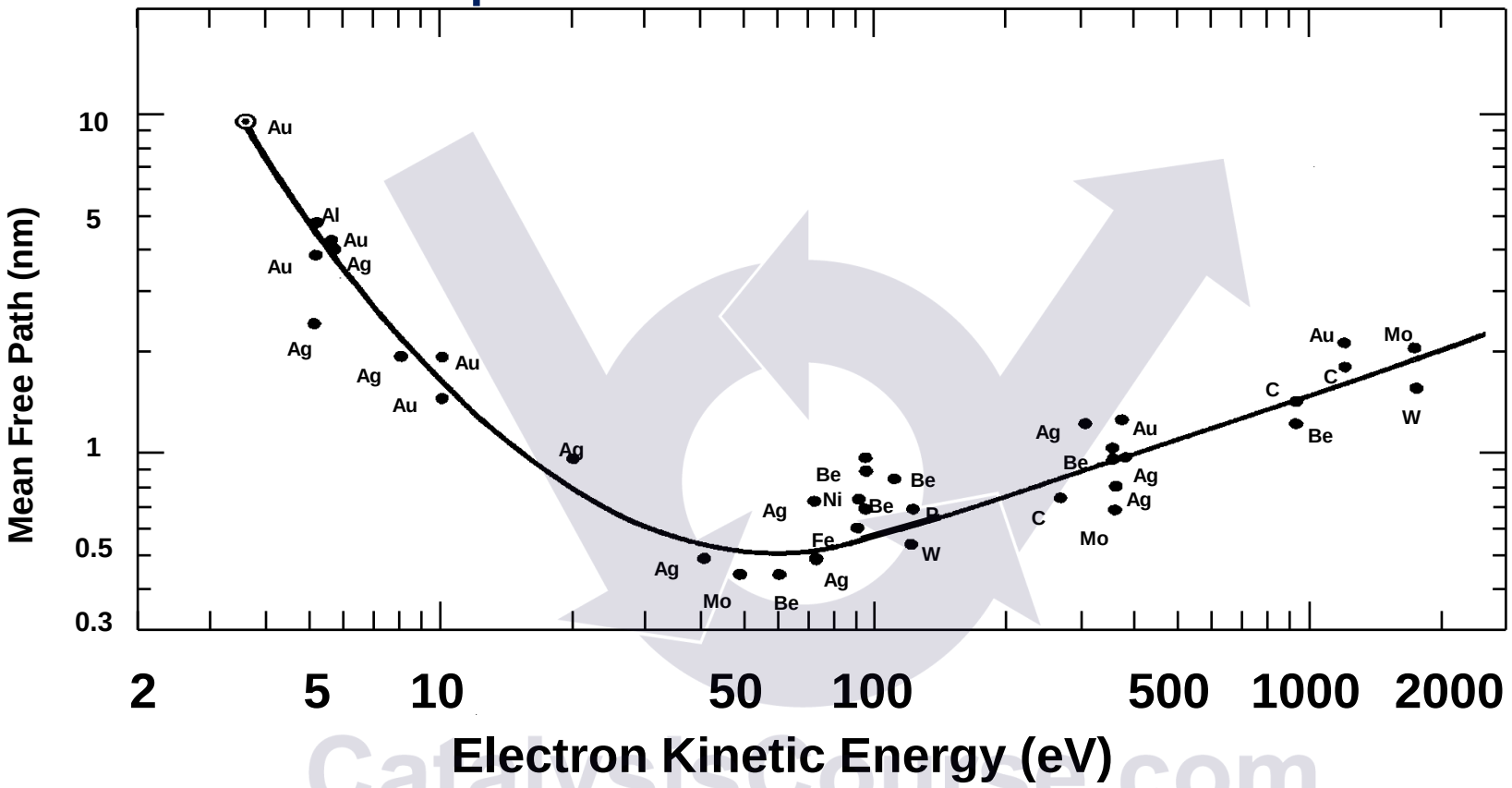


Electrons and ions cannot travel far…..

the mean free path of electrons in metals:



Hence, spectroscopies based on electrons (and ions) of not too high energy (below a few keV) are surface sensitive and require measurement in vacuum

G.A. Somorjai, Chemistry in Two Dimensions, Surfaces, Cornell University Press, Ithaca, 1981.

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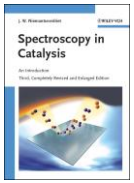
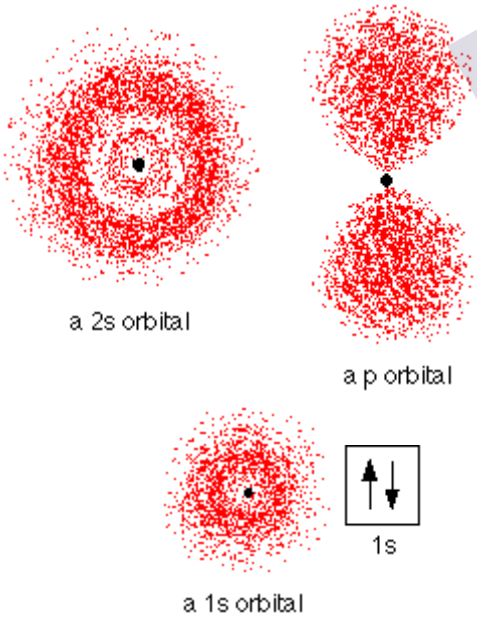
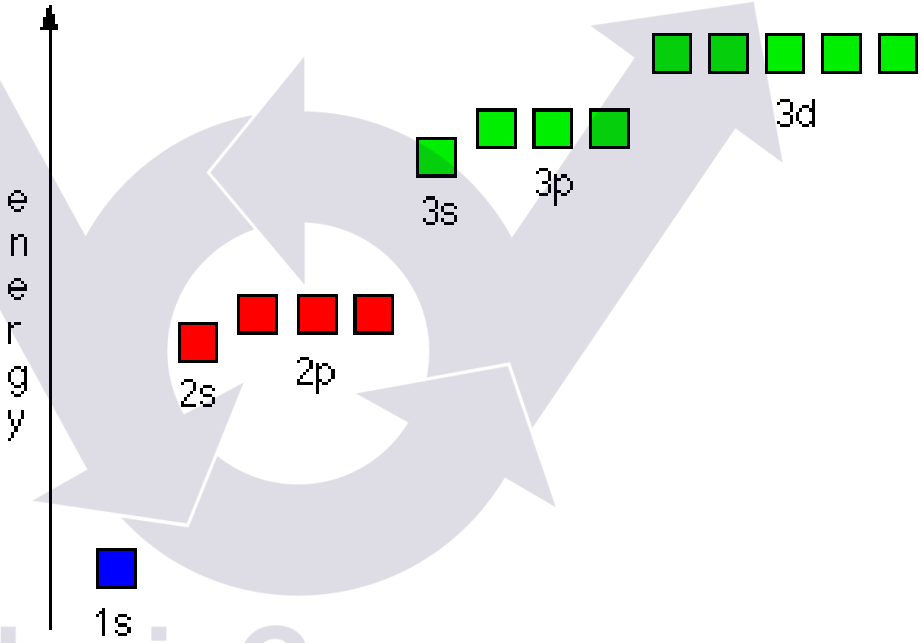
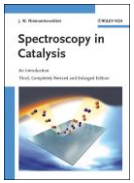


Electrons in Atoms

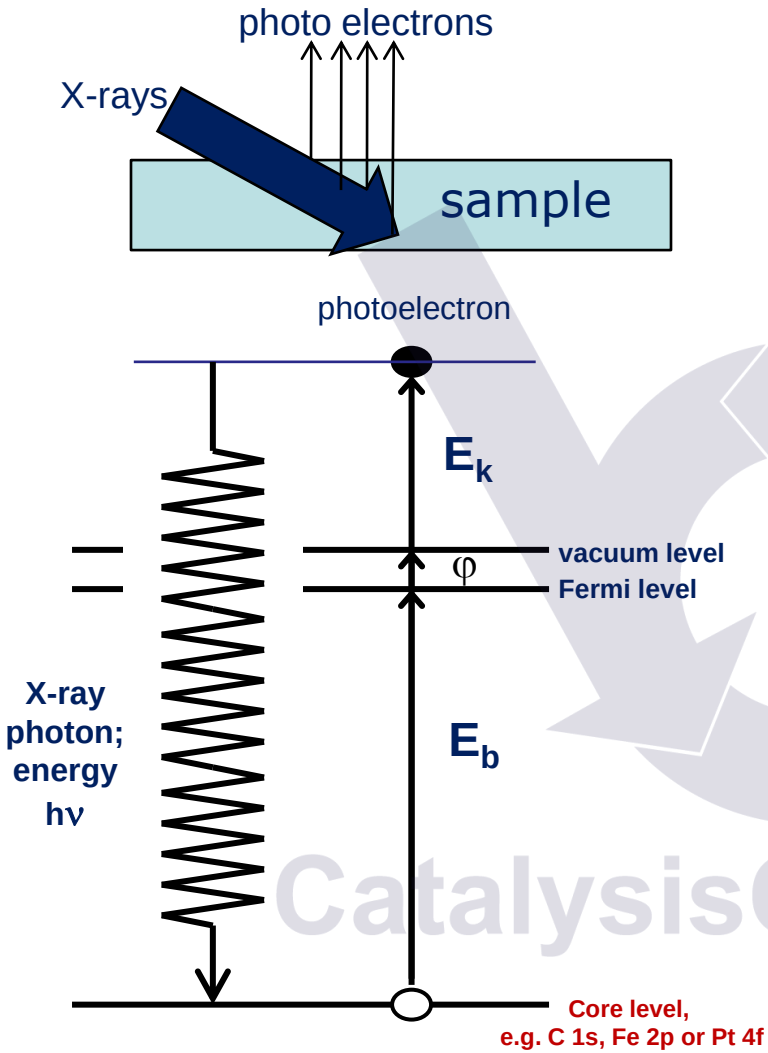




Electron orbital energies (binding energies) are **element specific**



X-ray Photoelectron Spectroscopy (XPS)



The photo emission process

$$E_b = h\nu - E_k - \varphi$$

- E_b: binding energy
- $h\nu$: X-ray energy; *known*
- E_k: kinetic energy *measured*
- φ: work function spectrometer *known*

Binding energies are

- element specific
- sensitive to
  - oxidation state
  - electronegativity

XPS is characteristic of the surface region

In XPS, binding energies are always referred to the Fermi level; as sample and spectrometer are in electrical contact, both are the same; the work function, φ, is that of the spectrometer

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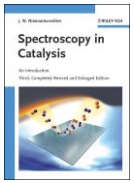
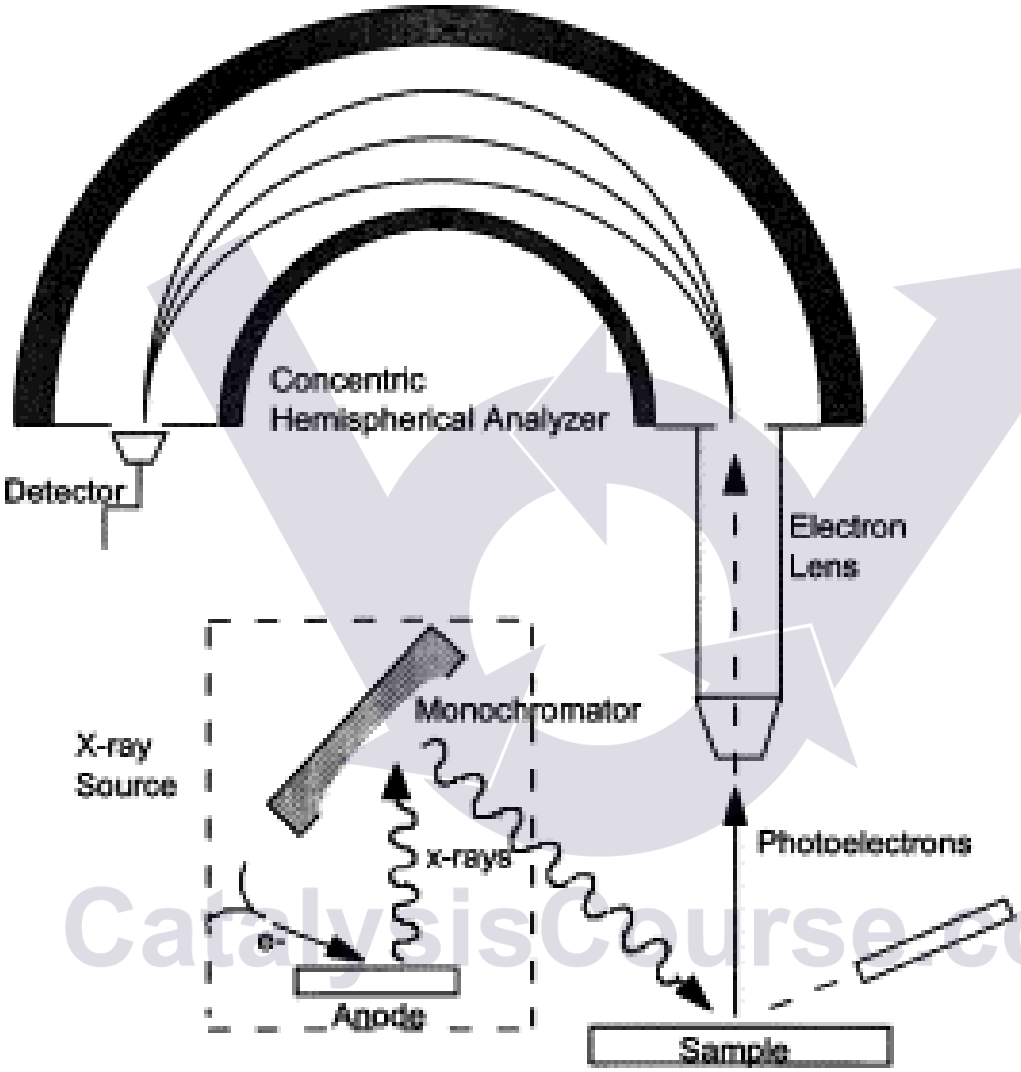


XPS Equipment



Standard X-ray source
(twin anode)
Mg Kα (1253.6 eV)
Al Kα (1486.6 eV)

Encyclopedia of Materials: Science and Technology
K. H. Jürgen Buschow, et al. (Eds) Elsevier 2007

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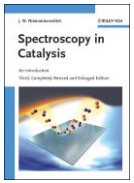

XPS peak nomenclature

$l = 0\ 1\ 2\ 3$

$s\ p\ d\ f$

orbital momentum

$4f_{7/2}$

$n = 0, 1, 2, 3, 4, 5$

main quantum number

$j = l \pm ½$

total momentum

$2j+1$ electrons

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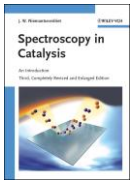
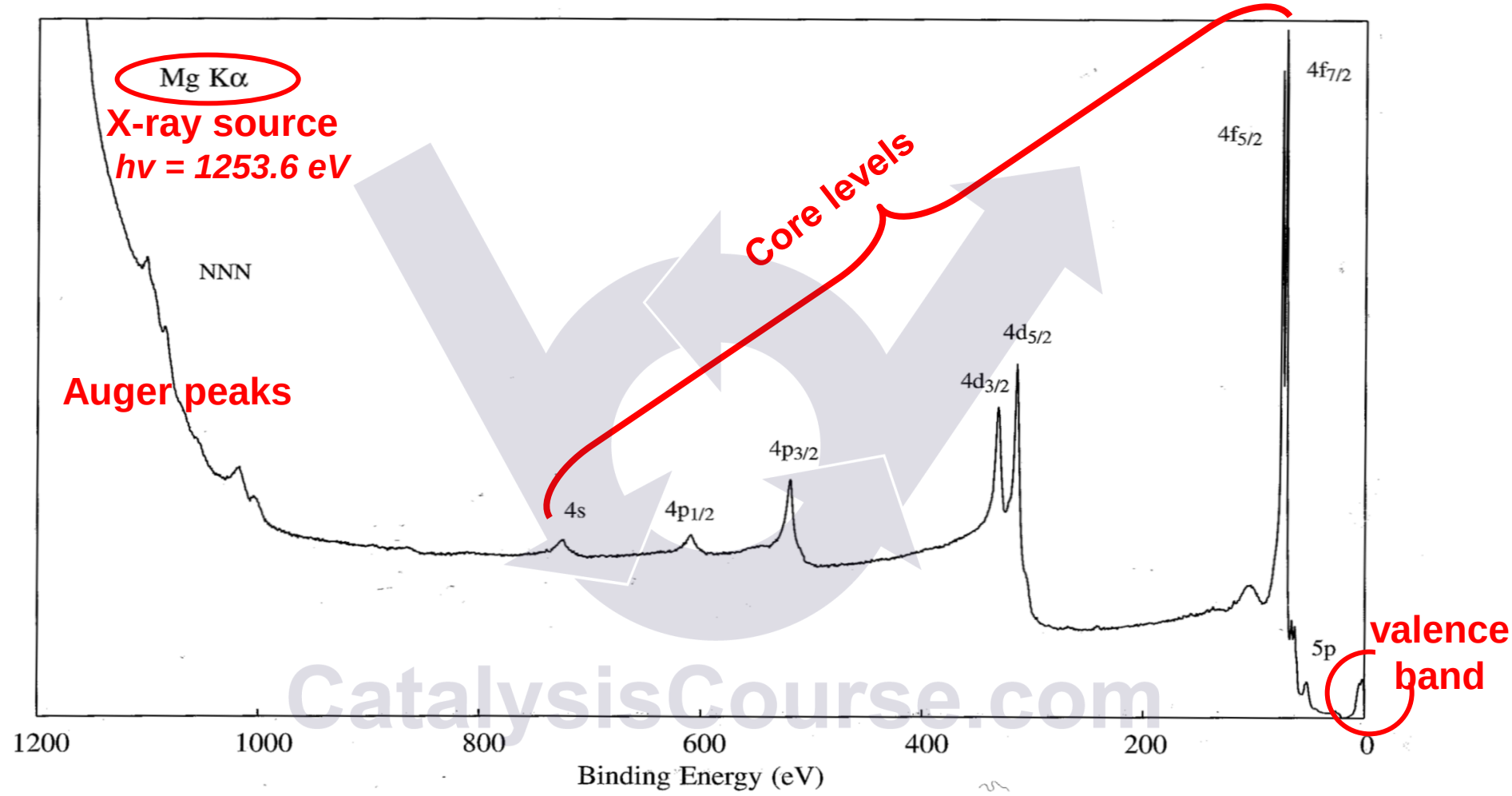
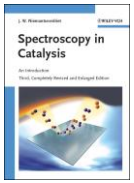


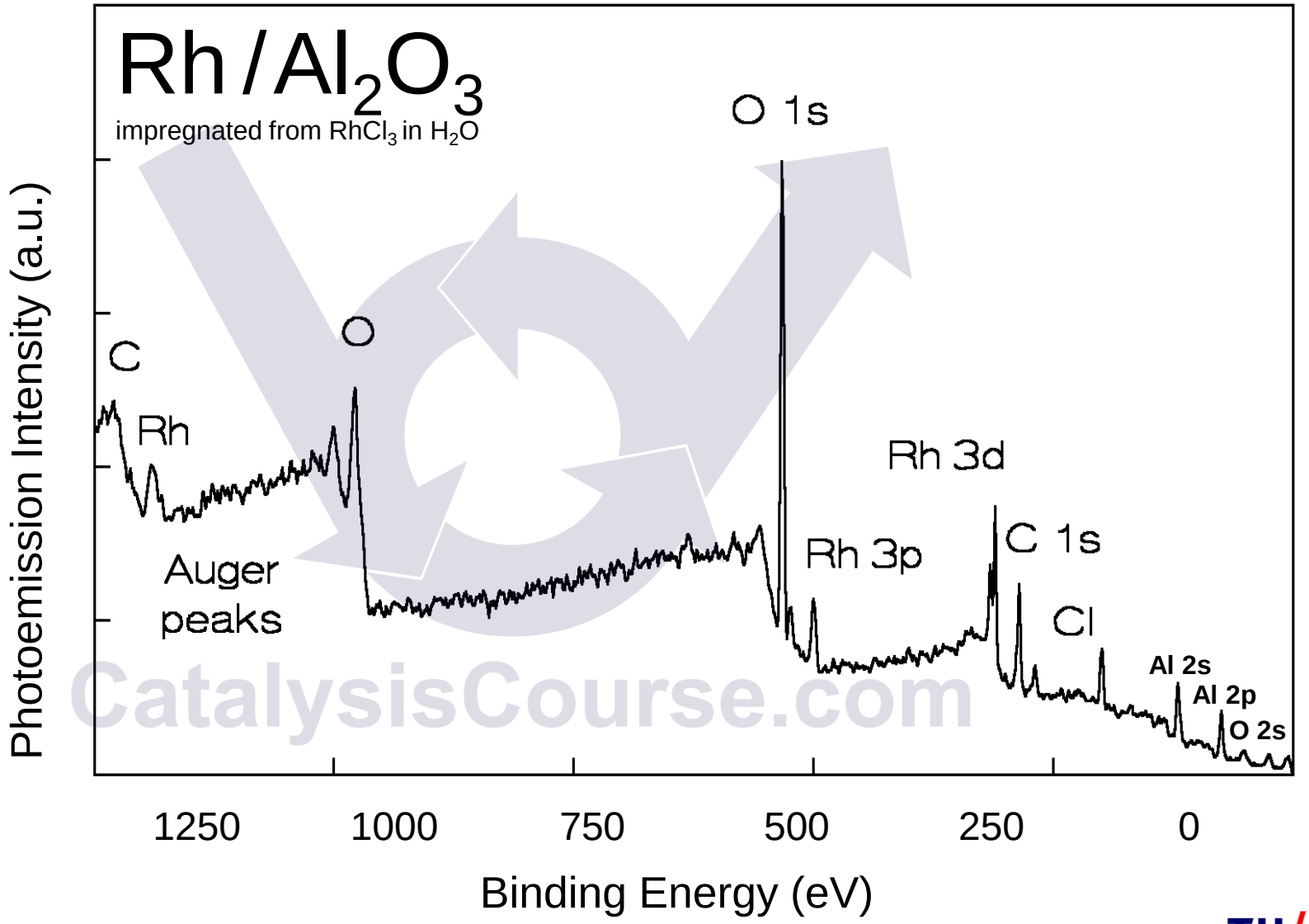
XPS wide scan of platinum



$$E_b = h\nu - E_k$$



XPS: Element Specific



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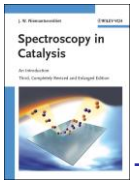
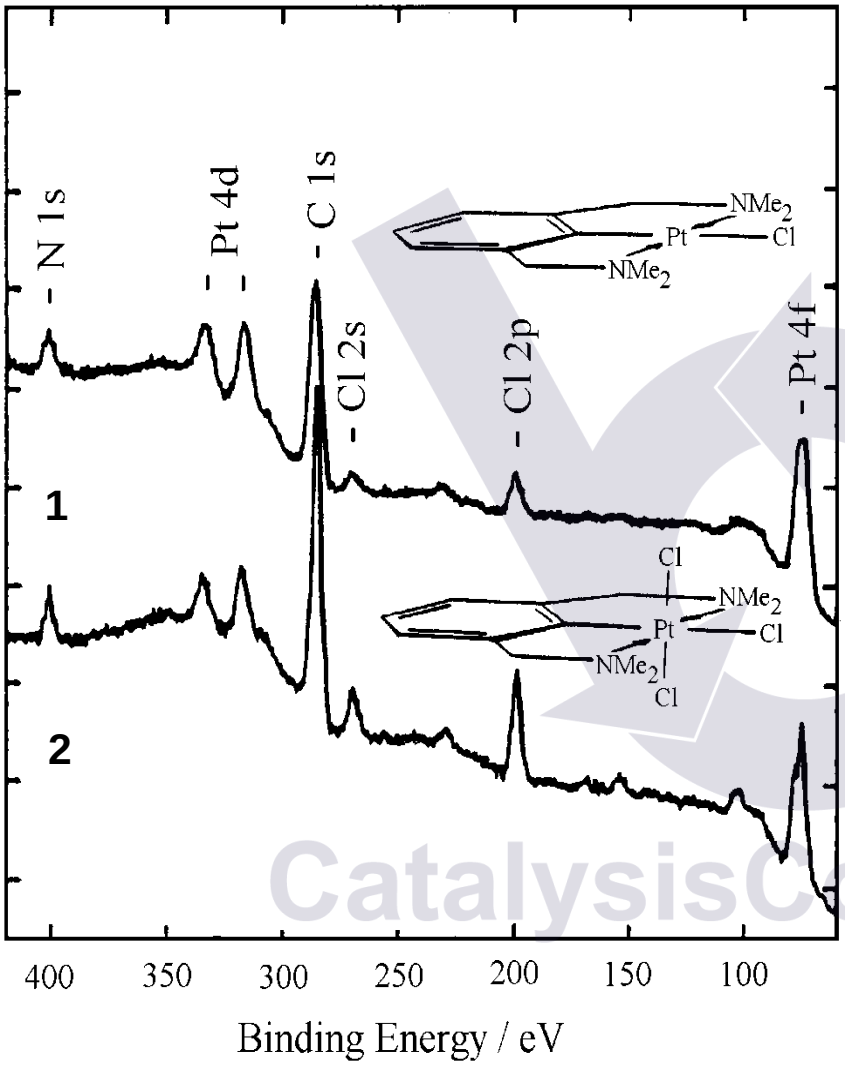
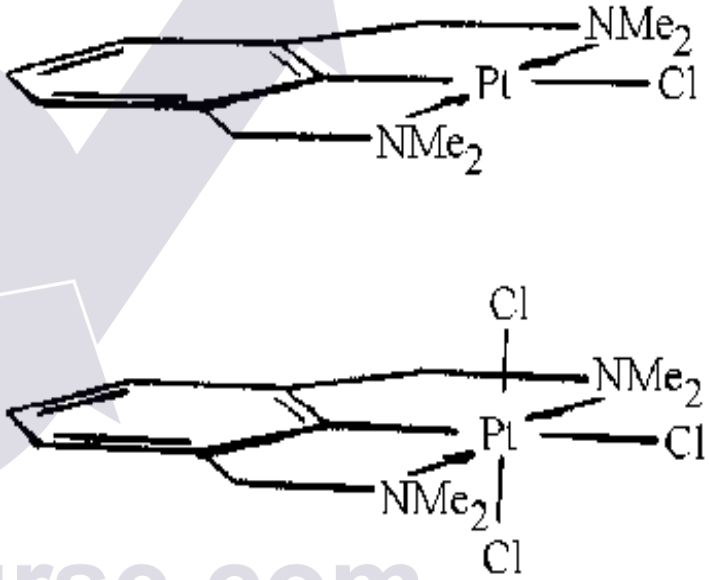


X-ray Photoelectron Spectroscopy (XPS) element specific



Homogeneous Pt catalyst, contains Pt, Cl, N, and C:



J.C. Muijsers, J.W. Niemantsverdriet, I.C.M. Wehman, D.M. Grove and G. van Koten, Inorg. Chem. 31 (1992) 2655-2658

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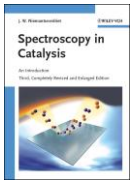
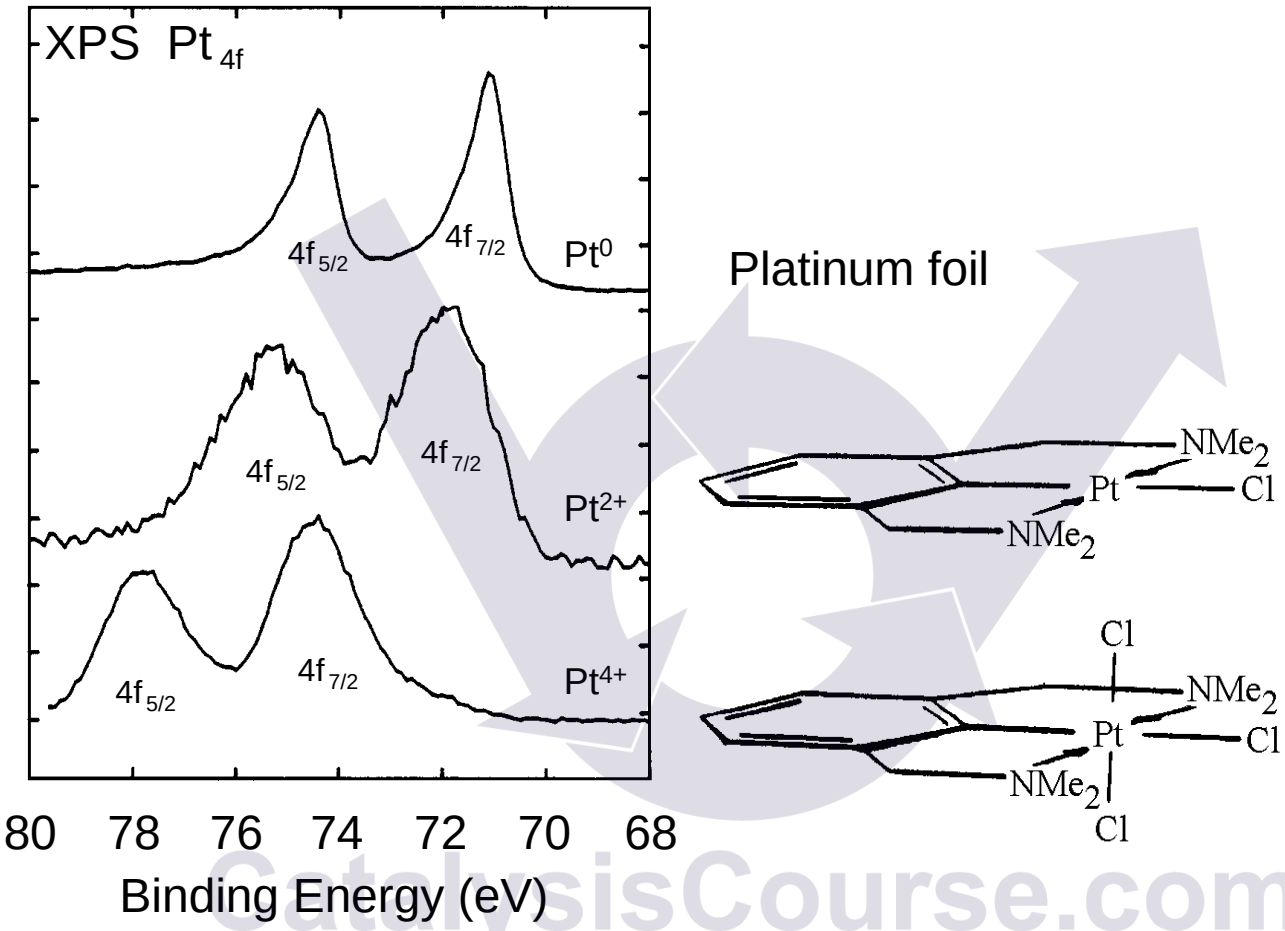


XPS: Oxidation states from chemical shifts



For many XPS peaks the binding energy increases with oxidation state (chemical shift)

J.C. Muijsers, J.W. Niemantsverdriet, I.C.M. Wehman, D.M. Grove and G. van Koten, Inorg. Chem. 31 (1992) 2655-2658

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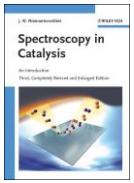
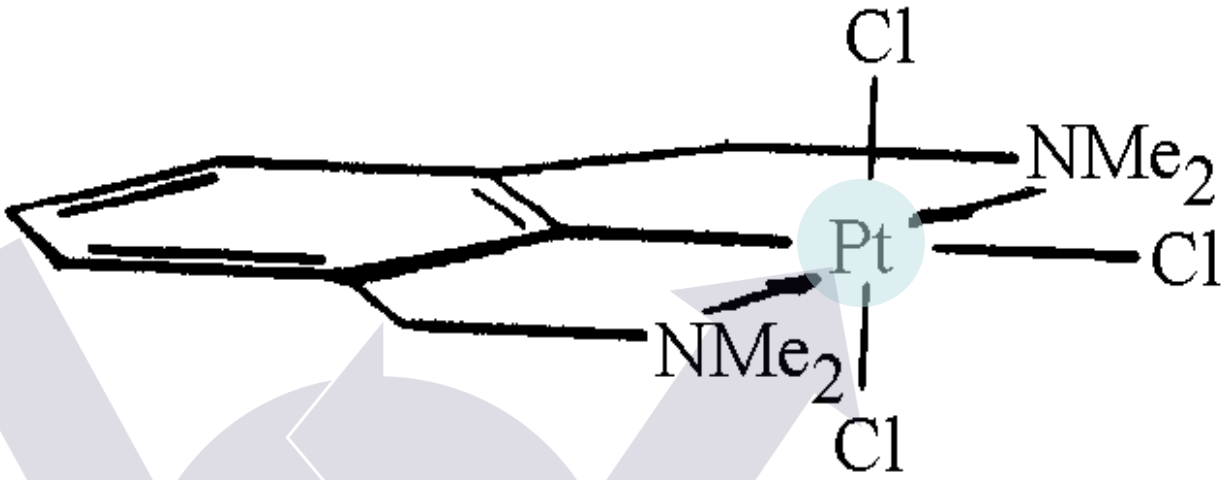


XPS: the chemical shift



$$E_b^i = k\,q_i + \sum_j \frac{q_j}{r_{ij}} + E_b^{ref}$$

XPS binding energy

charge on the atom

proportionality constant

sum of the Coulomb contributions from the neigbours at distance r_{ij} (Solid state physics: the Madelung Sum)

reference energy (e.g. the metal)

Charge potential model (Siegbahn)

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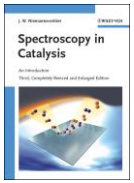
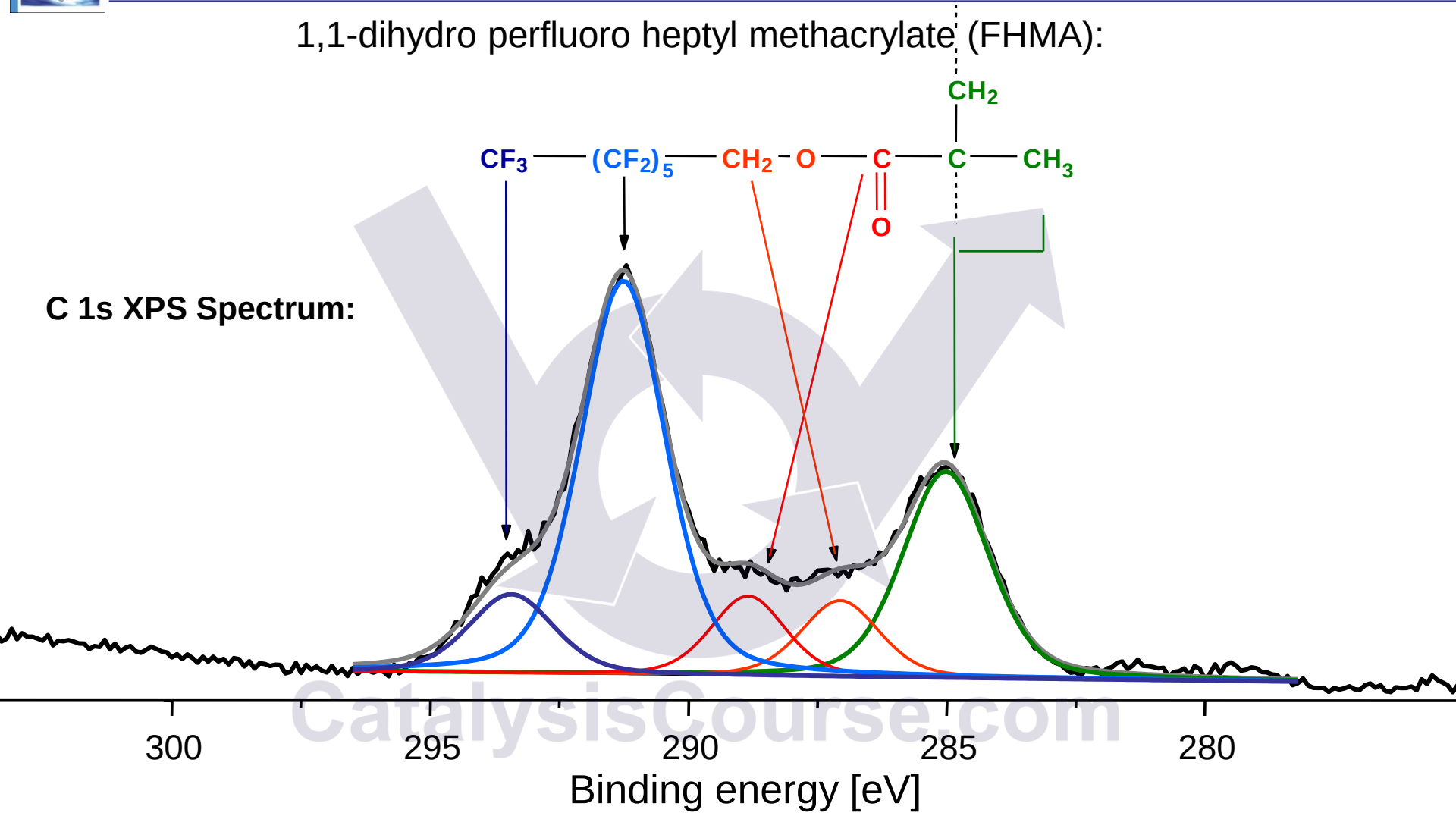


X-ray Photoelectron Spectroscopy (XPS)

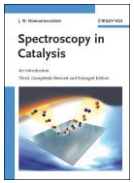
binding energy reflects the electronegativity of neighbours

1,1-dihydro perfluoro heptyl methacrylate (FHMA):

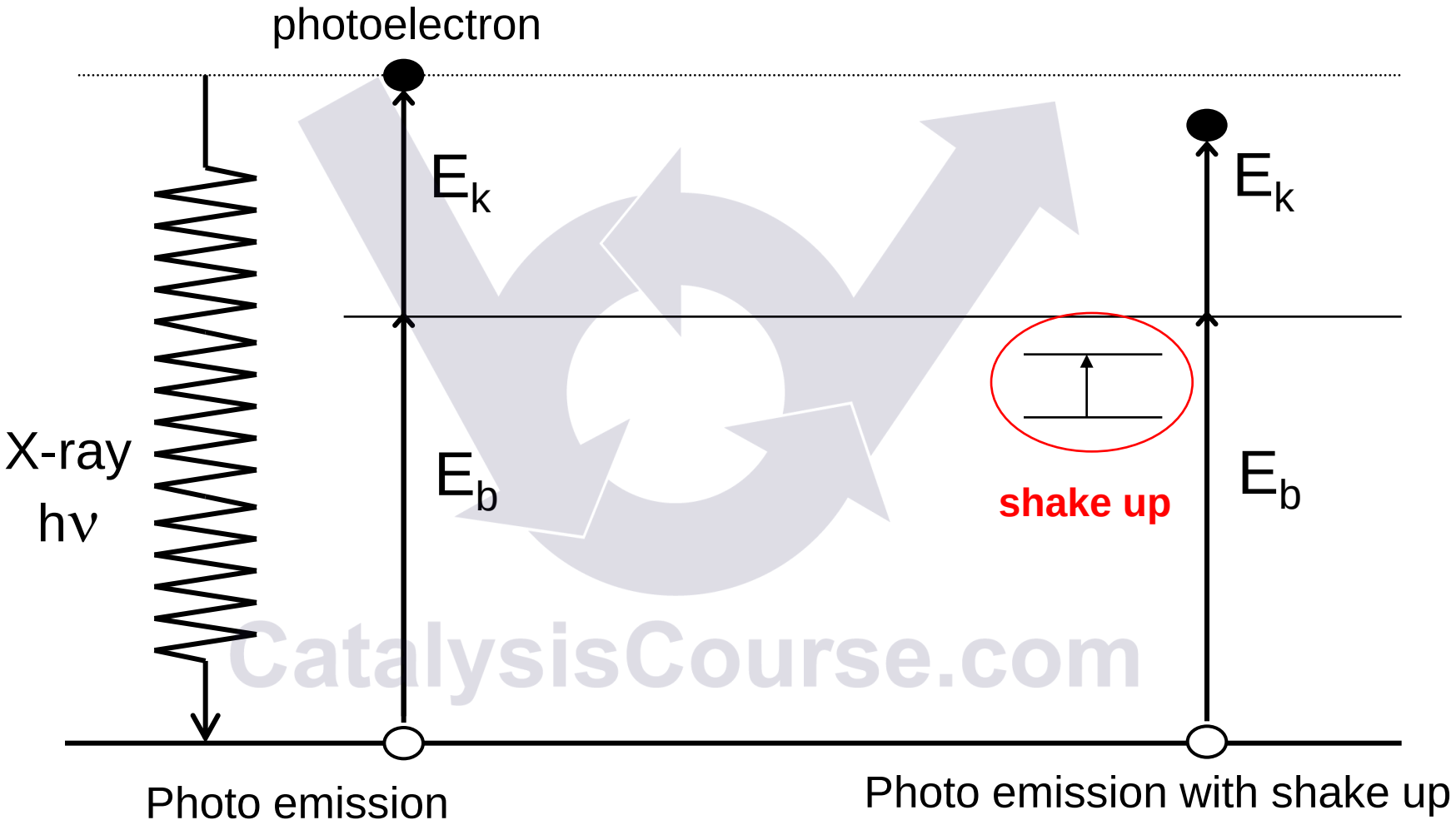


Every carbon is recognizable in the XPS spectrum

R.D. van de Grampel, W. Ming, A. Gildenpfennig, W. van Gennip, J. Laven, J.W. Niemantsverdriet, H.H. Brongersma, G. de With, R. van der Linde, Langmuir 20 (2004) 6344.



Shake up peaks may accompany the main peaks and have diagnostic value



$E_b = h\nu - E_k$

appears higher

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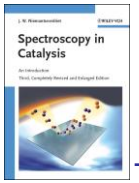
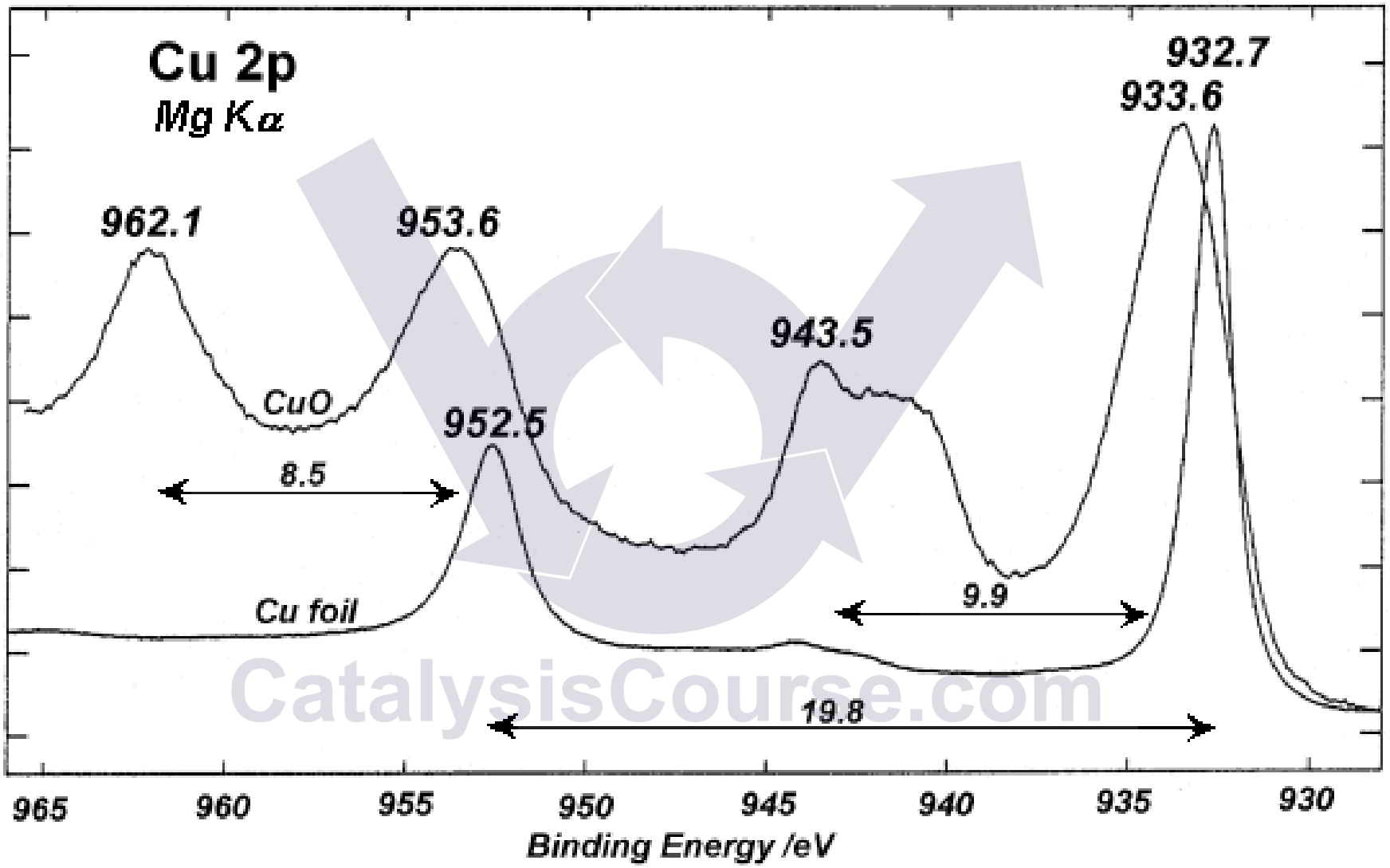
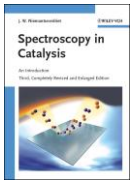


Shake up structures: diagnostic value

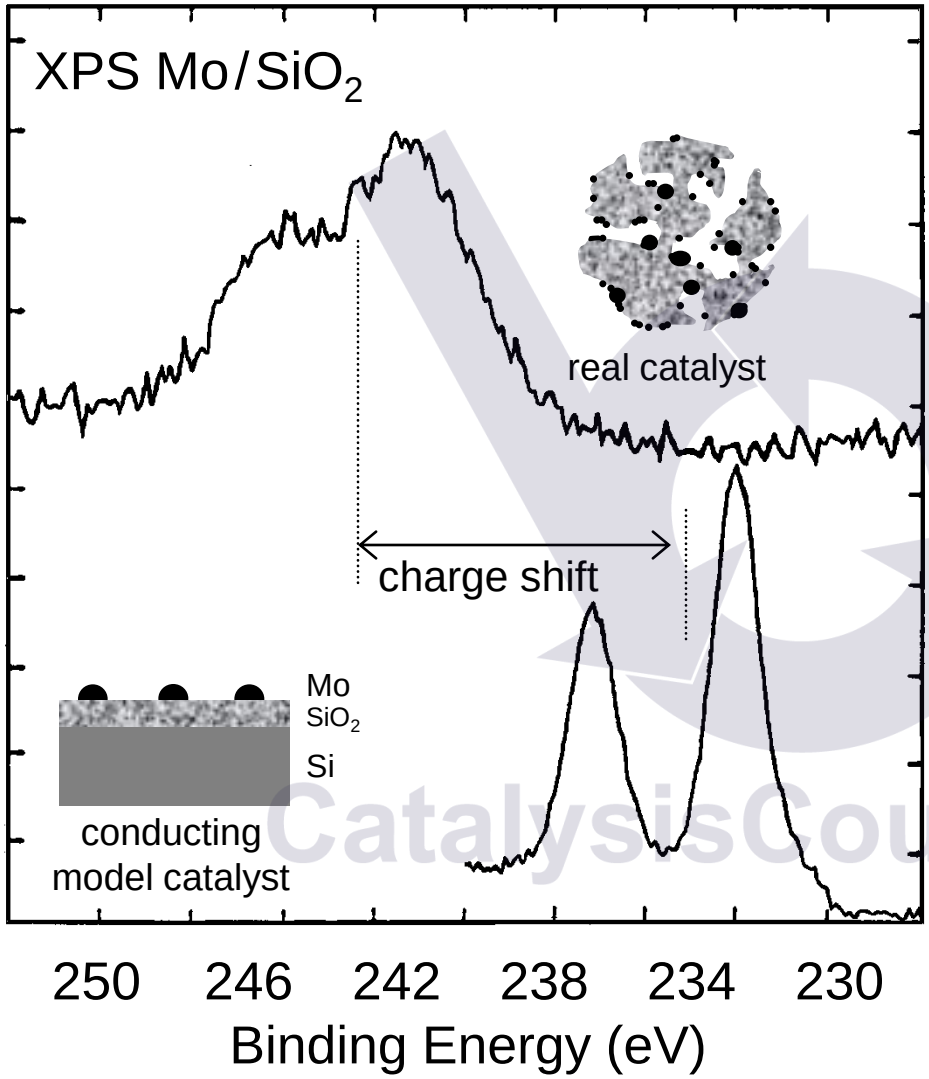


Shake up is prominent in XPS of oxides of Fe, Co, Ni, Cu



XPS of Catalysts: Charging

homogeneous or differential



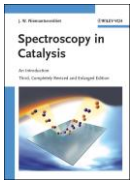
Charging shifts and broadens XPS peaks

Correct the shift via standards

- use the C 1s of contamination; it should be at 284 eV
- catalyst support; Si 2p of SiO_2 should be at 103.4 eV
- evaporated Au deposit

or

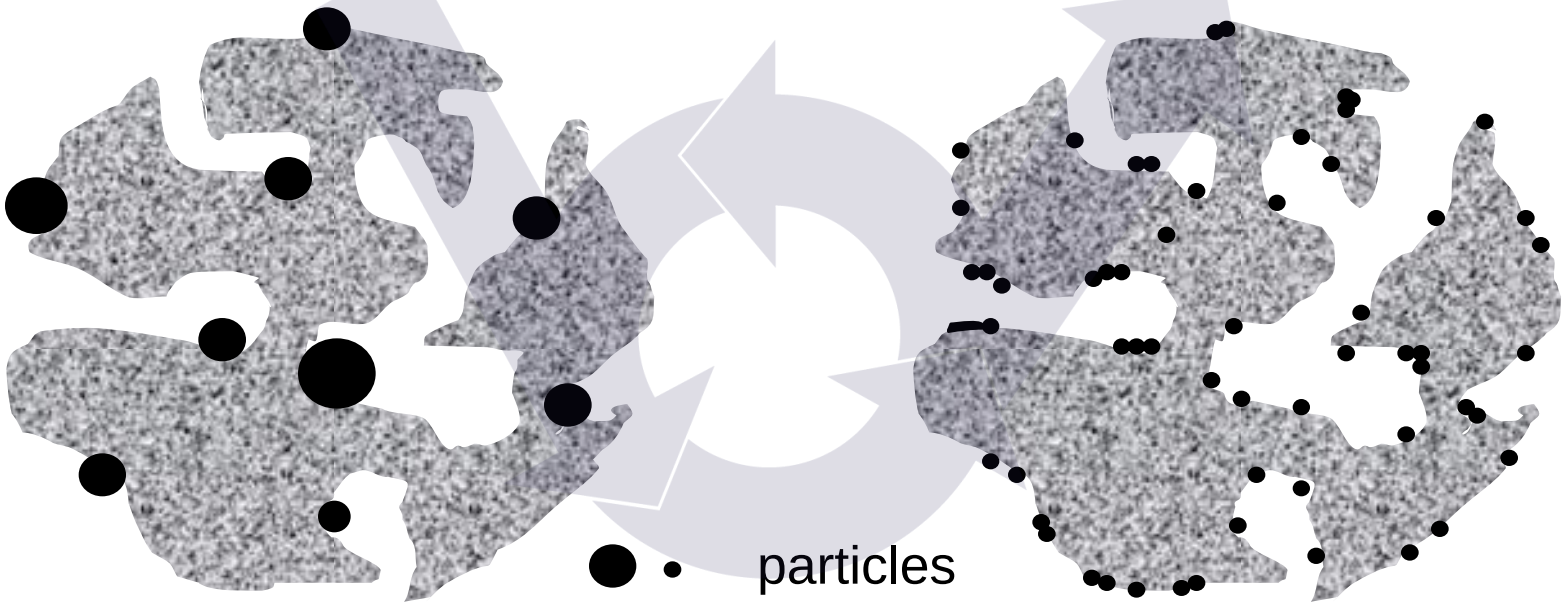
Prevent charging by using a flood gun of low energy electrons



XPS intensities reflect the dispersion

Low dispersion

High dispersion



particles

support

$I_{particle} / I_{support}$ ***small***

$I_{particle} / I_{support}$ ***large***

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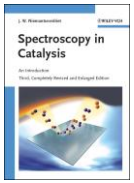
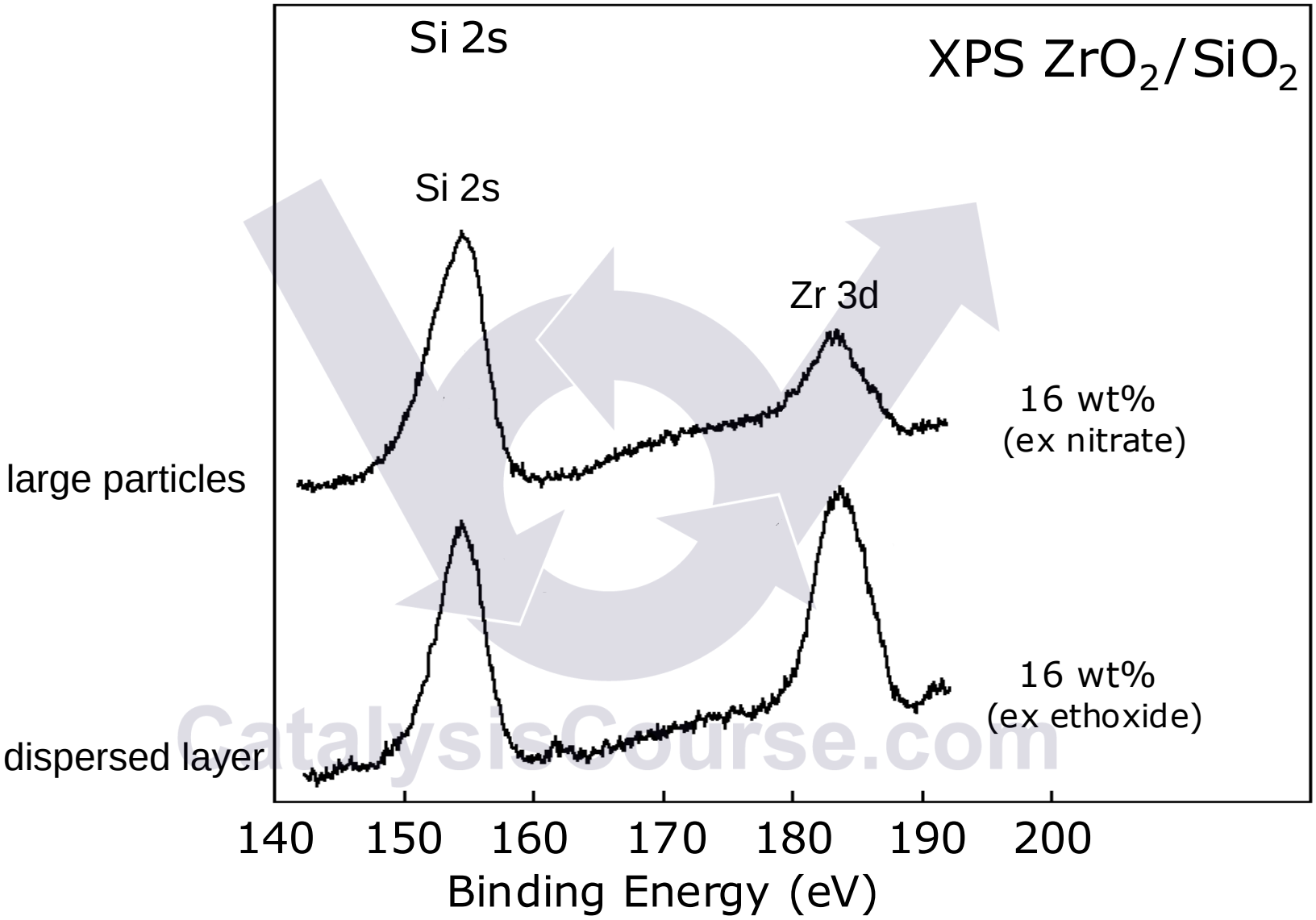


XPS intensities reflect the dispersion



A.C.Q.M. Meijers, A.M. de Jong, L.M.P. van Gruijthuijsen and J.W. Niemantsverdriet, Appl. Catal. 70 (1991) 53.

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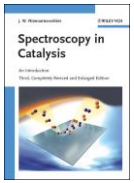


XPS

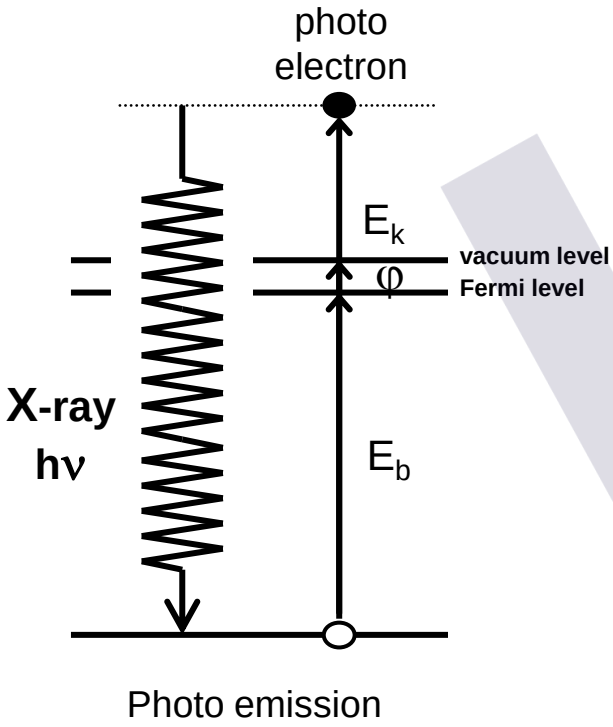
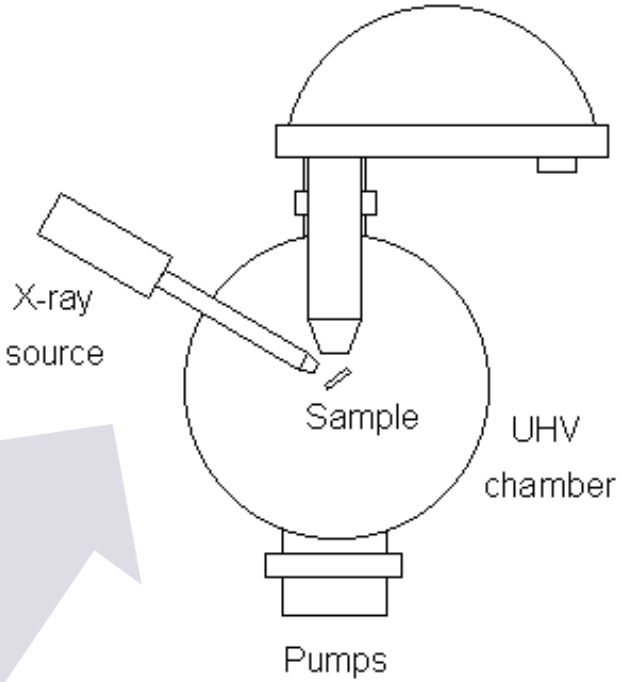


Photo emission

$$E_b = h\nu - E_k$$

known

measured



- **element specific**
- **sensitive to**
  - **oxidation state**
  - **electronegativity**
- **surface sensitive**
- **dispersion**
- **charge correction easy**
- **vacuum required**

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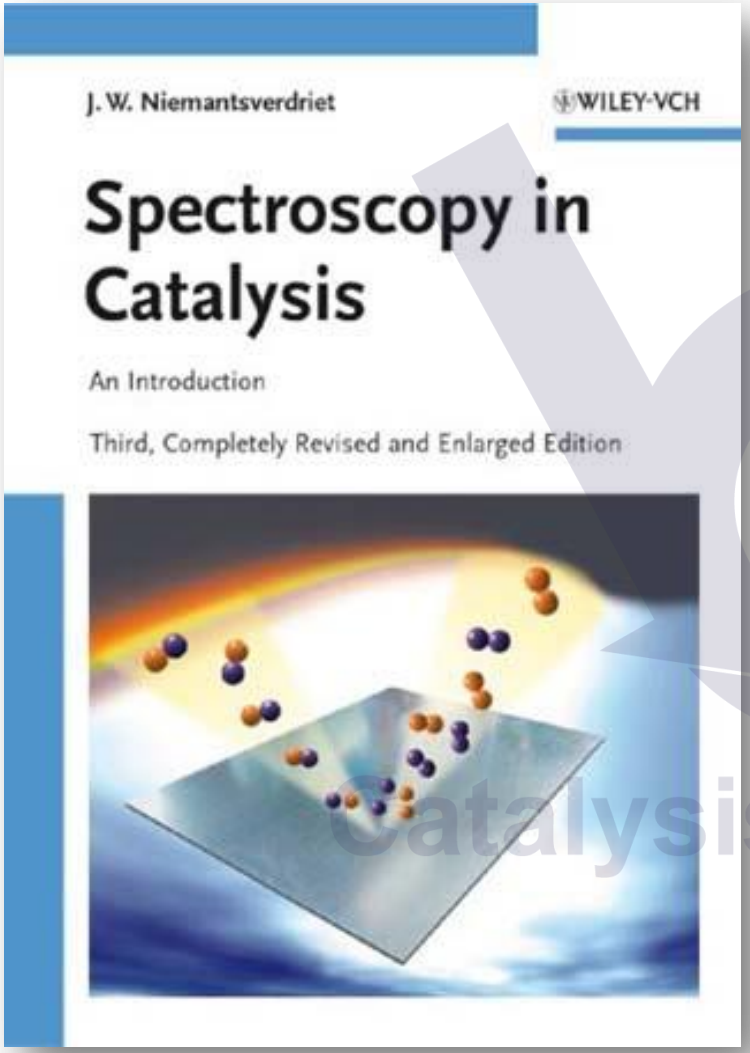
www.catalysiscourse.com



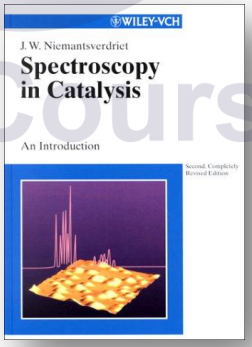
Read more about the Electron Spectroscopies

in Chapter 3 of

Spectroscopy in Catalysis: An Introduction, Third Edition

J. W. Niemantsverdriet

ISBN: 978-3-527-31651-9



Version 2000

gives many examples and references to the literature

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