Lecture **Materials Characterization III**
Winter term 2019/20
Part 2 (L. Grill)

Contact

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Physikalische Chemie

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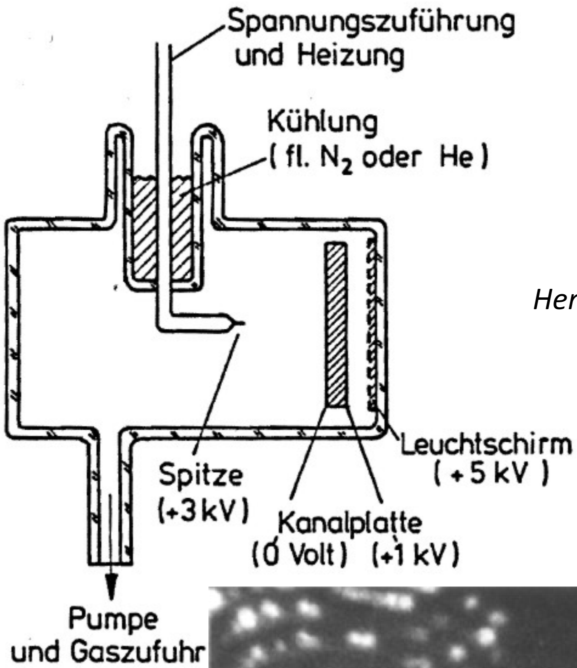
Universität Graz

VL	
15.1.	17:00 – 18:30
20.1.	14:00 – 15:30
21.1.	14:00 – 15:30
27.1.	14:00 – 15:30
28.1.	14:00 – 15:30

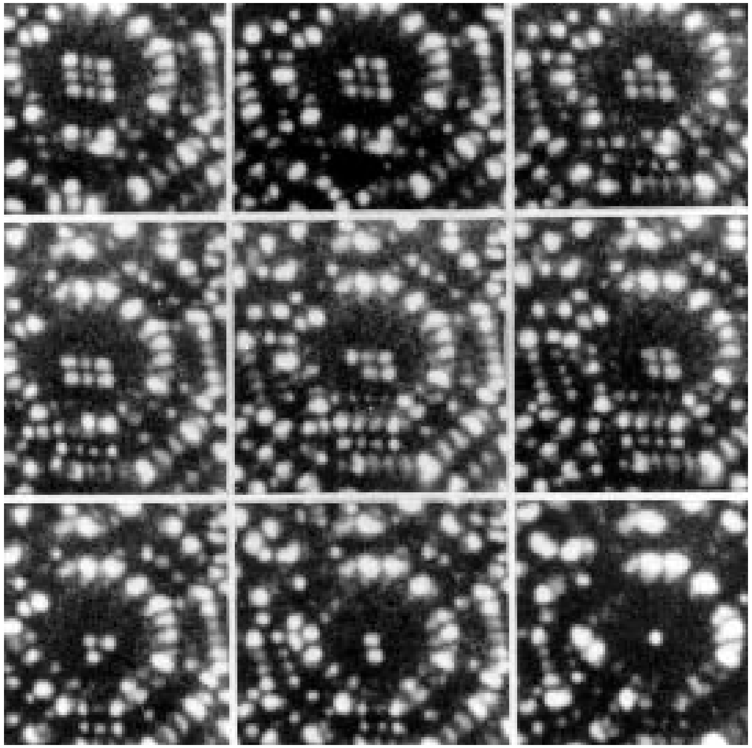
Contents

Field ion microscope

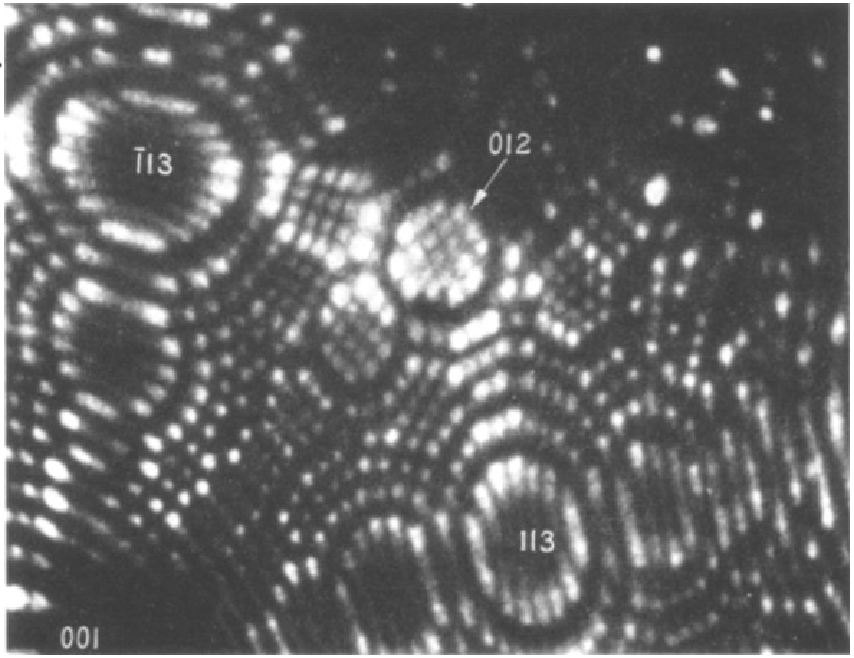


Henzler/Göpel: Oberflächenphysik des Festkörpers, Teubner

Ni_7Zr_2 tip



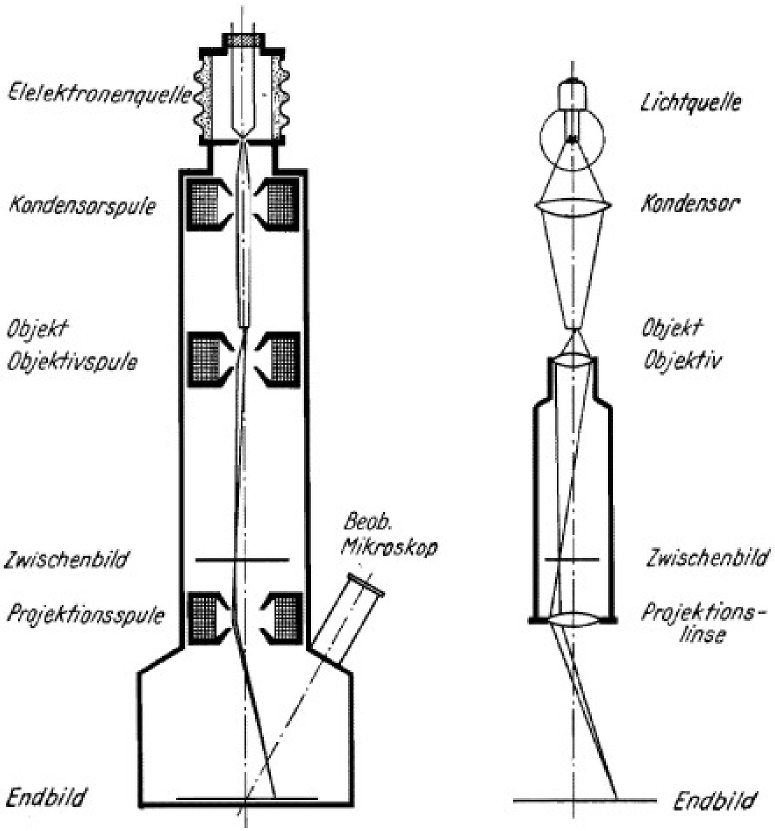
M. K. Miller et al. (Oakridge National Laboratory)



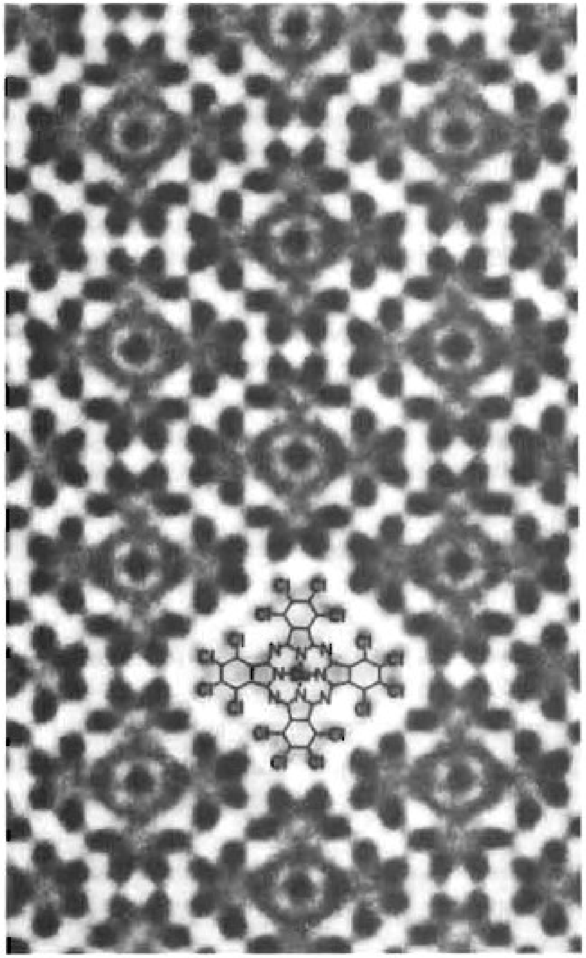
W tip

E. W. Müller, Z. F. Physik 156, 399 (1959)

Electron microscopy



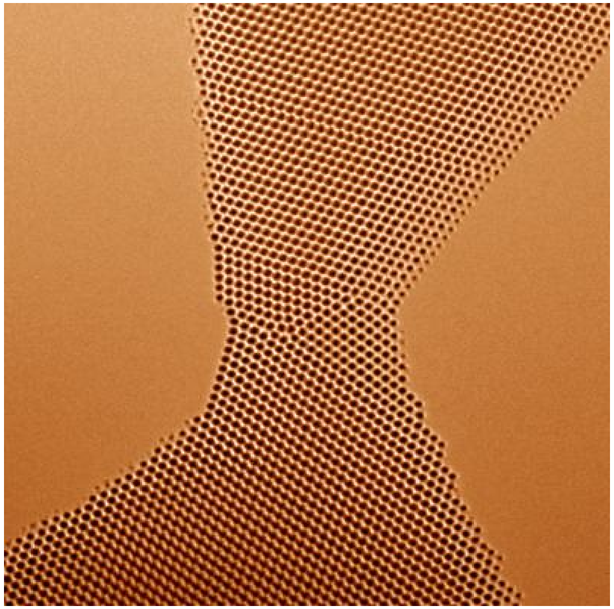
Single molecules
(500 keV microscope)



Physik, Gerthsen et al (Springer 1992)

Electron microscopy

Au nanobridge
(TEM)



Au nanobridge
(TEM)

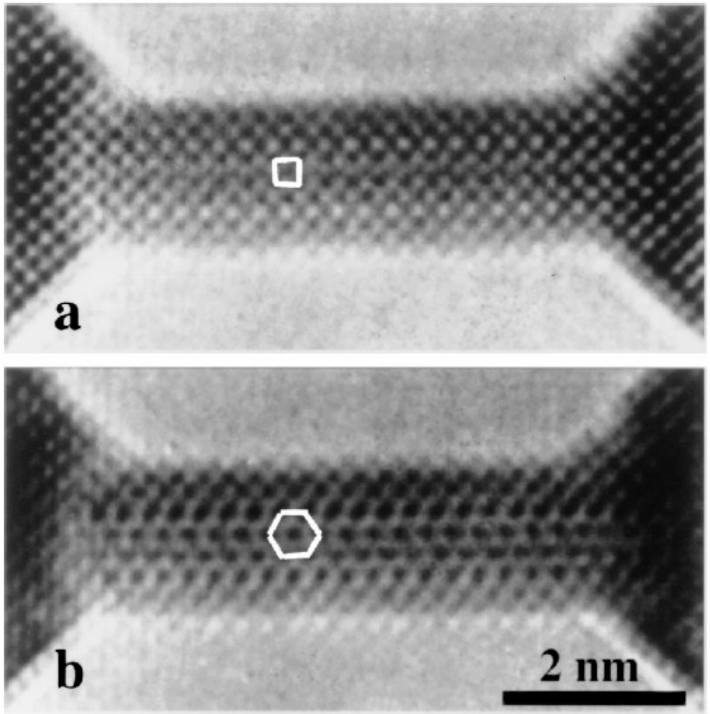
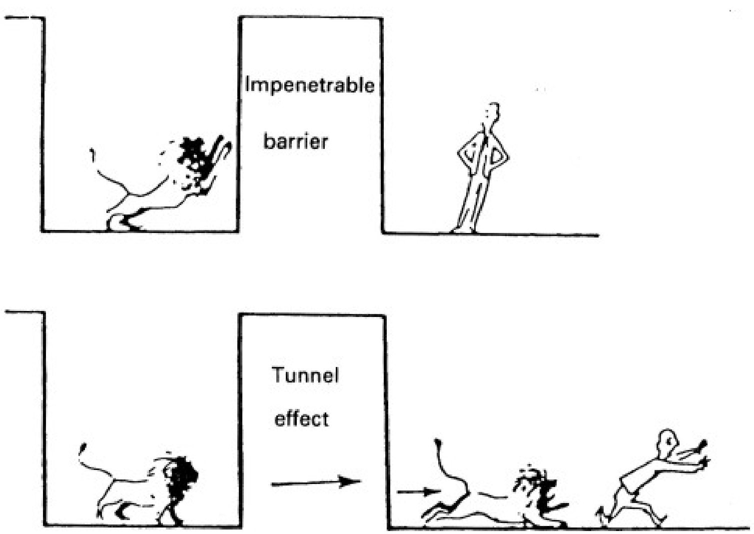


FIG. 2. Transmission electron micrographs of an NB 2 nm thick; obtained at the focuses of (a) 65 nm and (b) 55 nm. Note the square lattice in (a) and hexagonal one in (b).

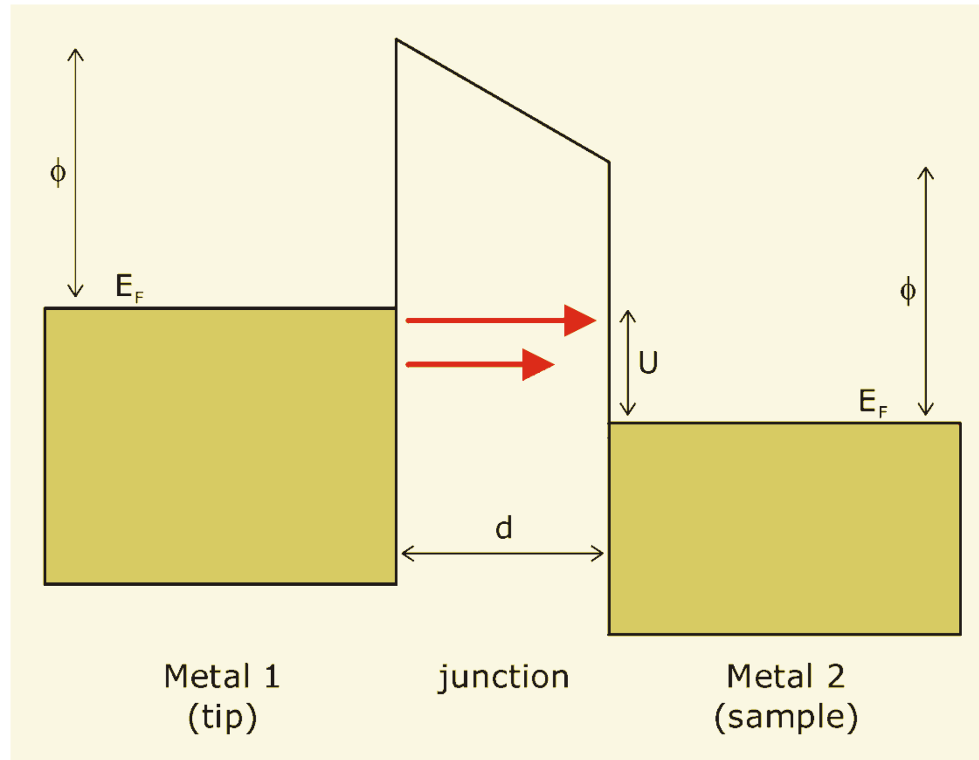
Y. Kondo et al., Phys. Rev. Lett. 79, 3455 (1997)

STM



B. Bleaney, Contemp. Phys. 25, 320 (1984)

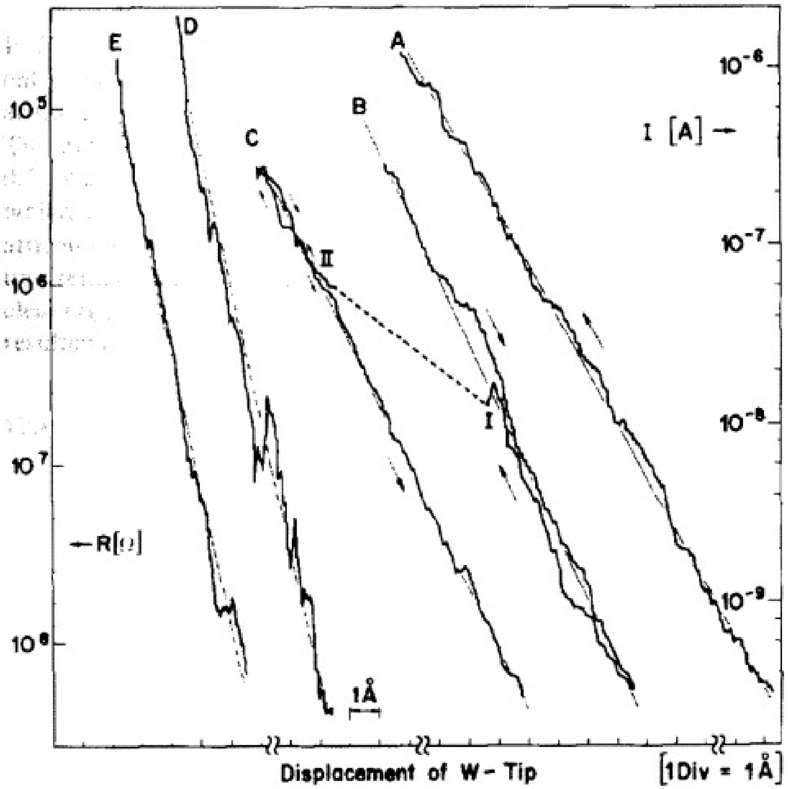
STM concept



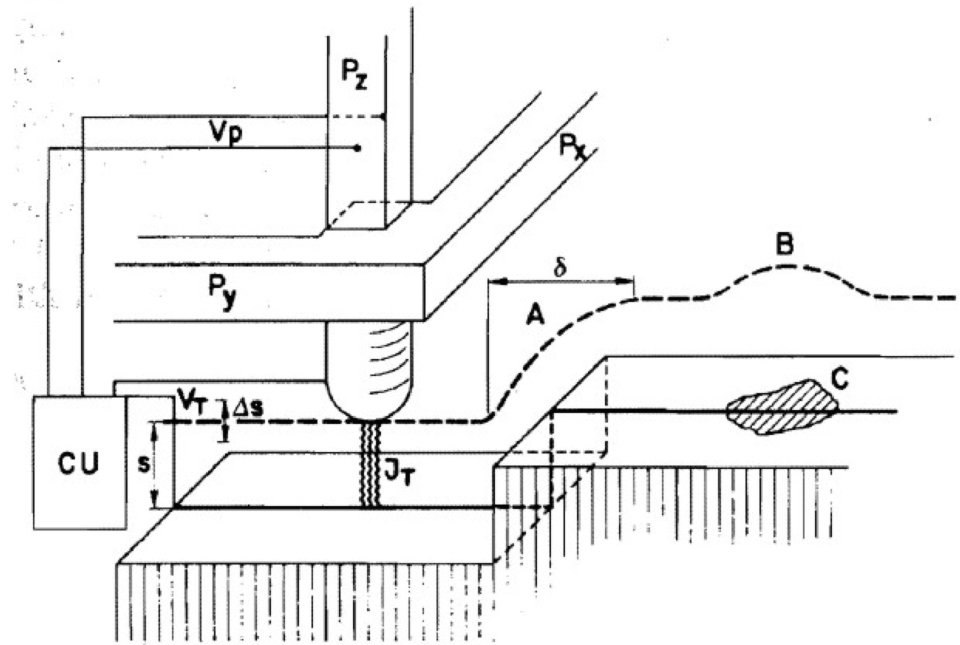
$$I \sim U \cdot e^{-2kd}$$

$$k = \frac{\sqrt{2m\Phi}}{\hbar}$$

Electron tunneling

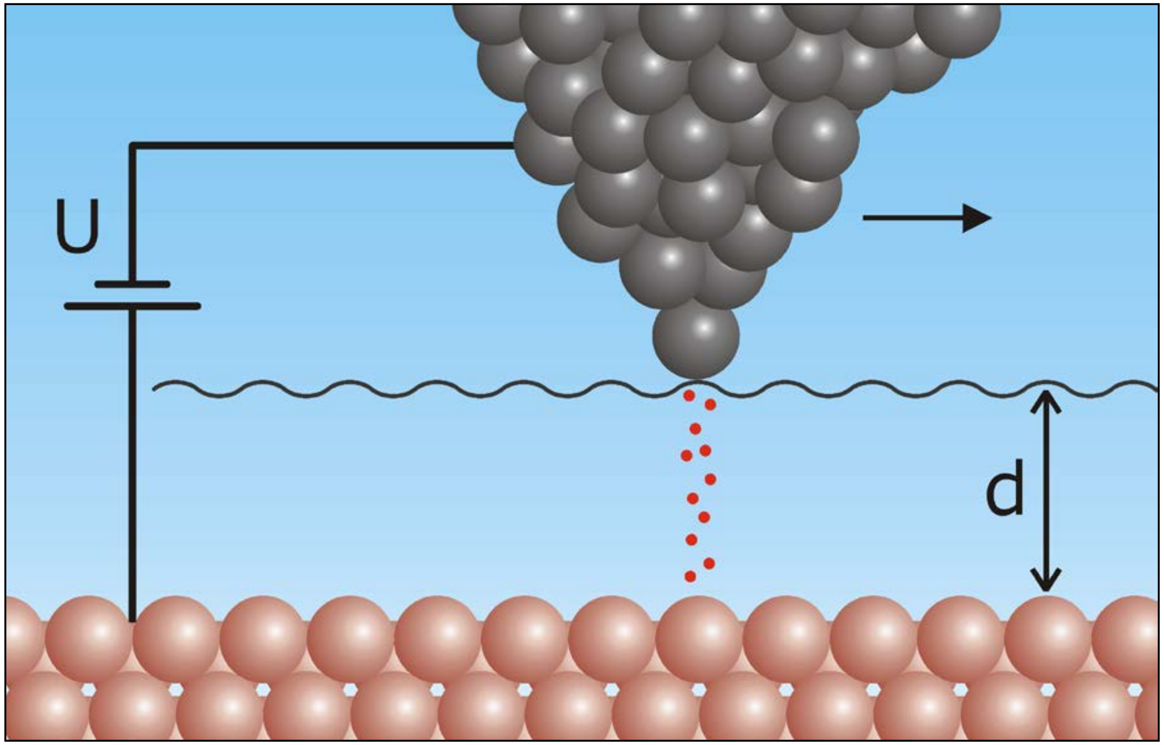


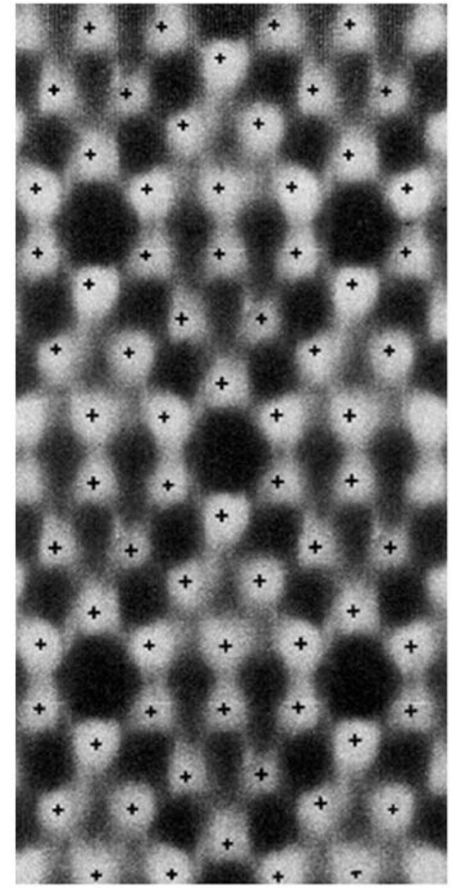
G. Binnig et al., Appl. Phys. Lett. 40, 178 (1982)



G. Binnig et al., Phys. Rev. Lett. 49, 57 (1982)

STM

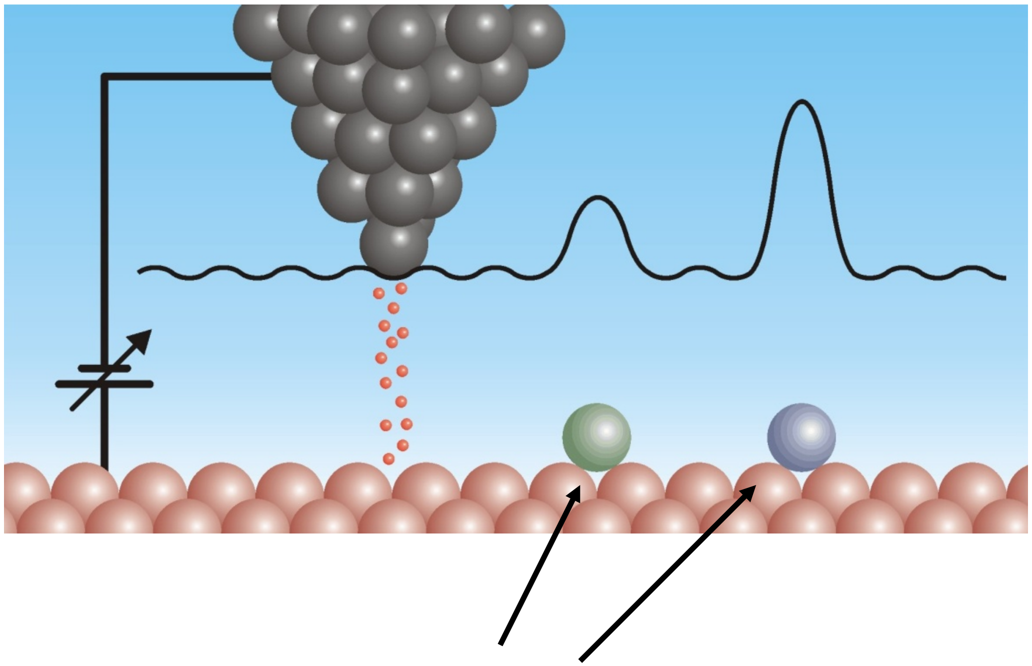




Si(111) 7x7 reconstruction

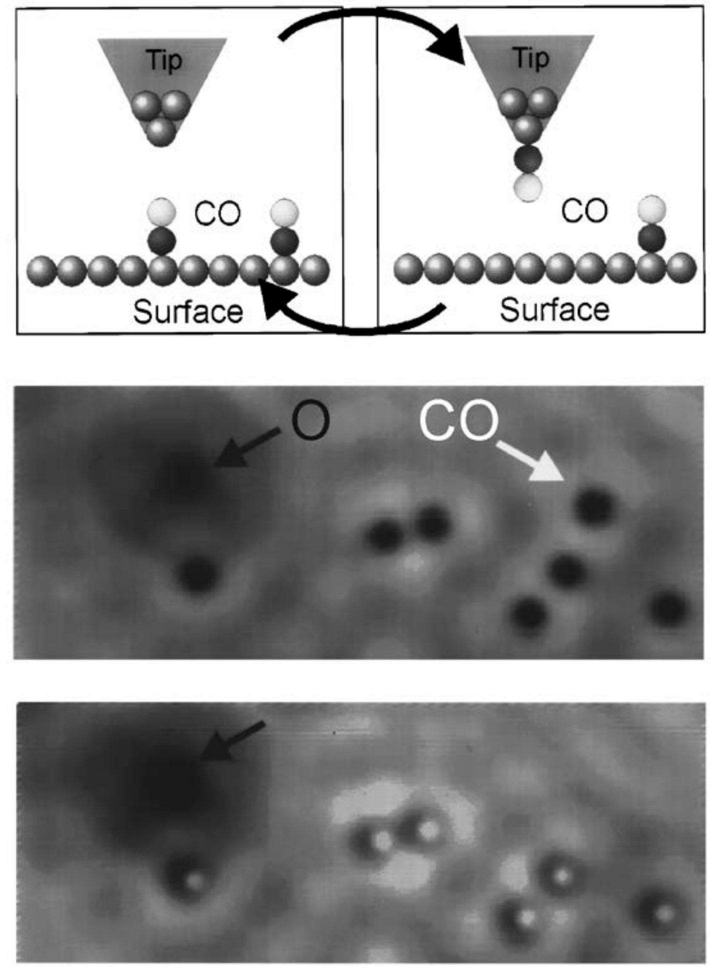
G. Binnig, H. Rohrer,
Ch. Gerber, and E. Weibel
Phys. Rev. Lett. **50**, 120 (1983)

„Chemical contrast“



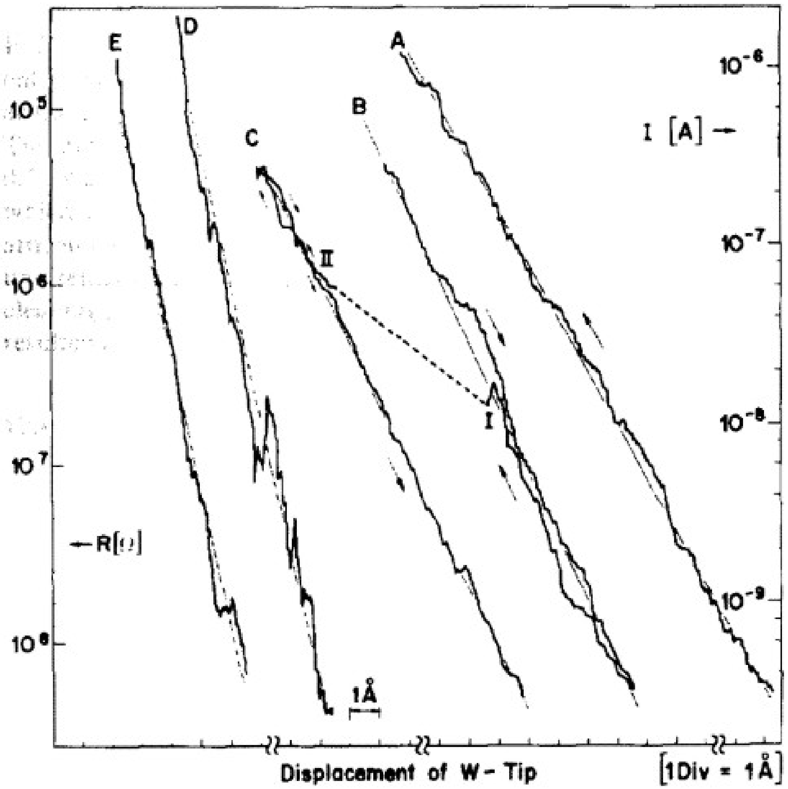
Different atomic/molecular species

Oxygen and CO on Cu(111)

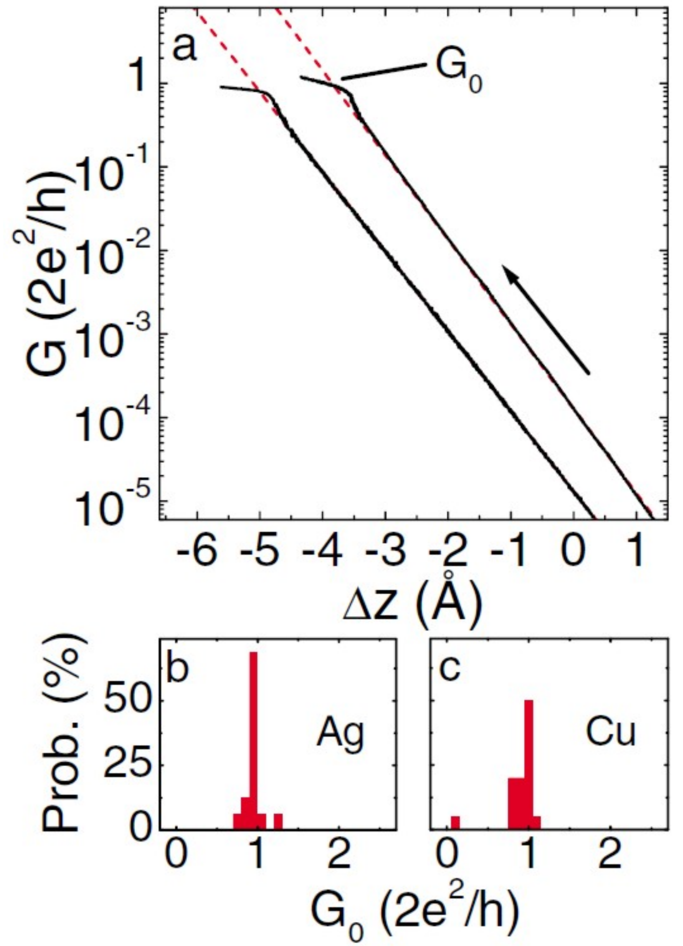


L. Bartels et al., APL 71, 213 (1997)

Point contact

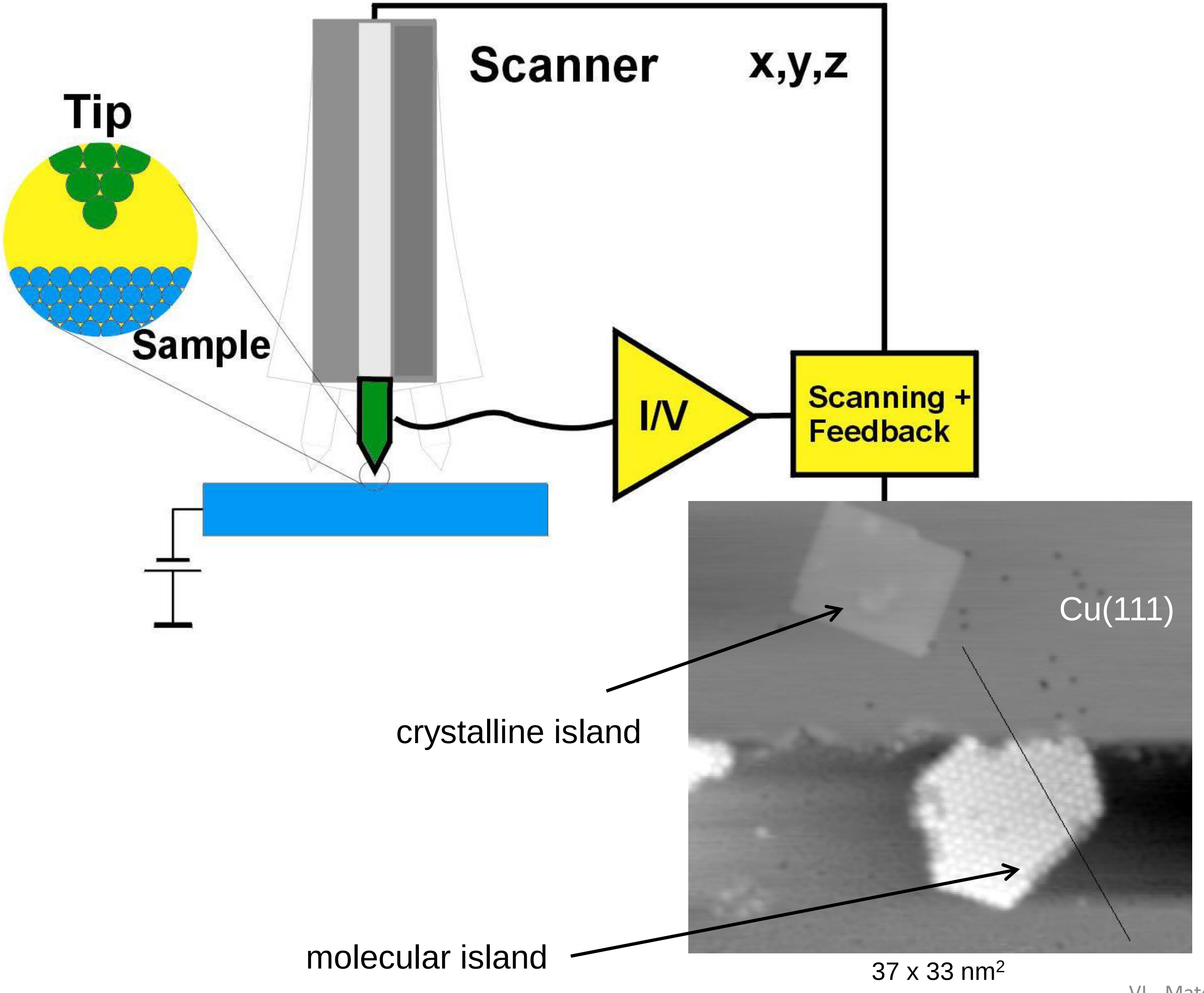


G. Binnig et al., Appl. Phys. Lett. 40, 178 (1982)



R. Berndt, Phys. Rev. Lett. 94, 126102 (2005)

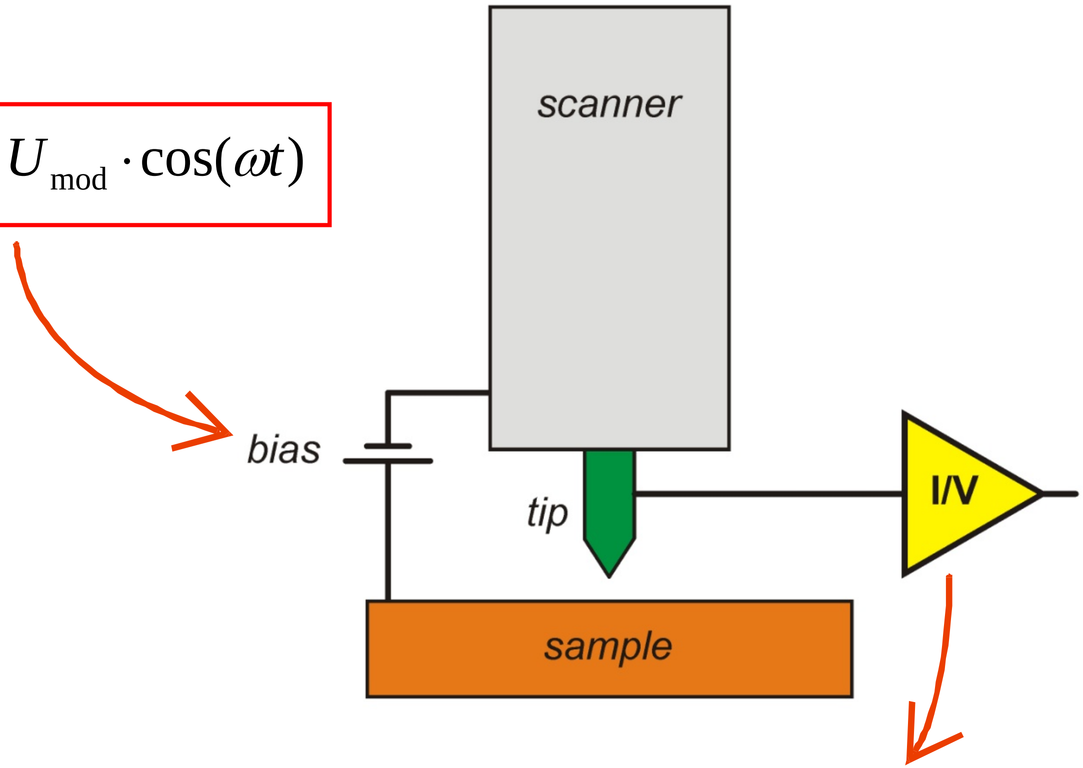
Feedback loop



Spectroscopy

$$\frac{dI}{dV} \approx D_s(E_F + eU)$$

$$U_o + U_{\mathrm{mod}} \cdot \cos(\omega t)$$



$$I = I_o + \frac{dI(U_o)}{dU} \cdot U_{\mathrm{mod}} \cdot \cos(\omega t) + \frac{d^2 I(U_o)}{dU^2} \cdot U_{\mathrm{mod}}^2 \cdot \cos^2(\omega t) + \ldots$$

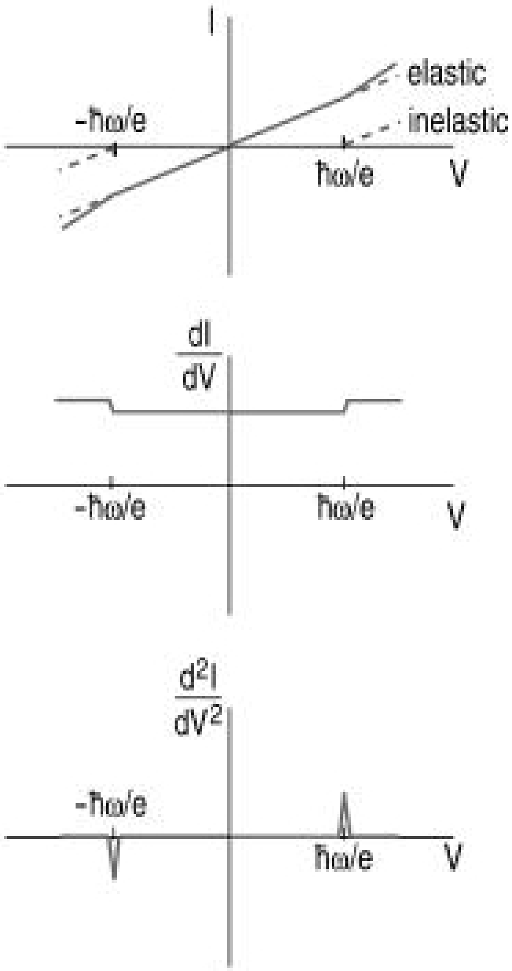
lock-in signal

$$\tfrac{1}{2}(1 + \cos(2\omega t))$$

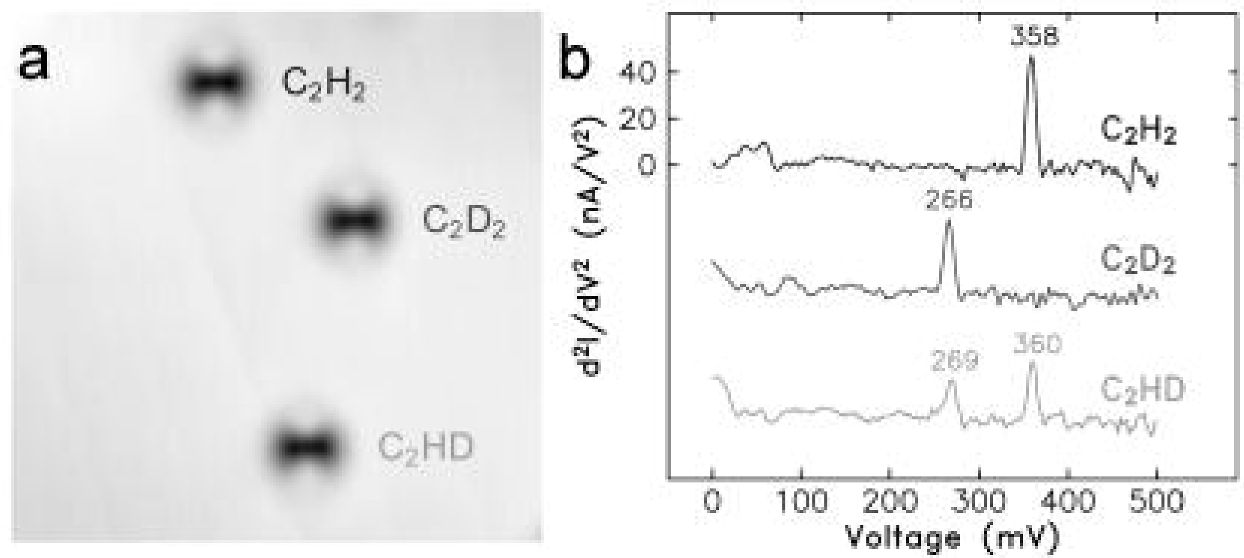
Vibrational Spectroscopy – chemical identification

Current signal: $$I = I_o + \frac{dI(U_o)}{dU} \cdot U_{\text{mod}} \cdot \cos(\omega t) + \frac{d^2 I(U_o)}{dU^2} \cdot U_{\text{mod}}^2 \cdot \underbrace{\cos^2(\omega t)}_{\frac{1}{2}(1+\cos(2\omega t))} + \ldots$$

double frequency



Acetylene (C_2H_2) molecules on Cu(100)

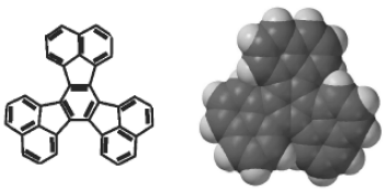


W. Ho, J. Chem. Phys. 117, 11033 (2002)

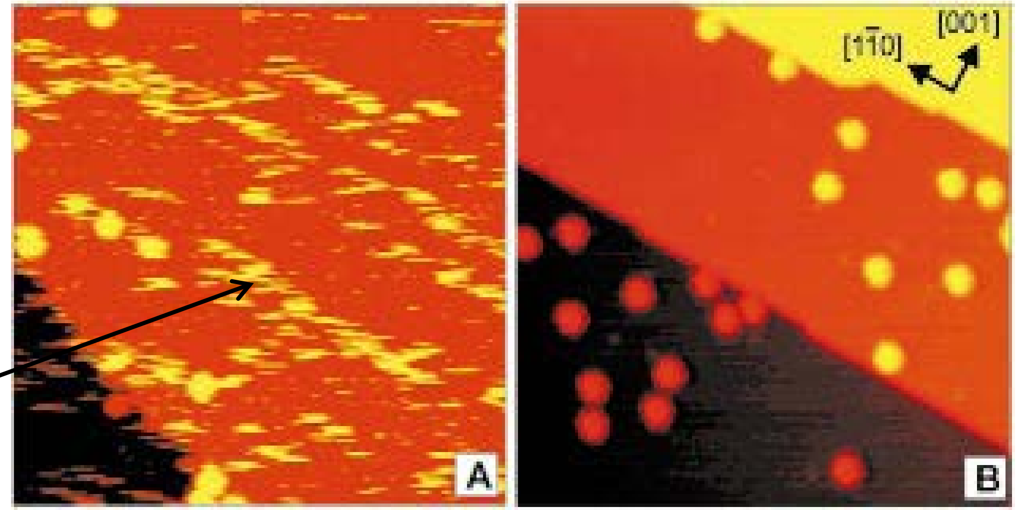
The role of the temperature: Required cooling

DC on Cu(110)

DC (decacyclene)

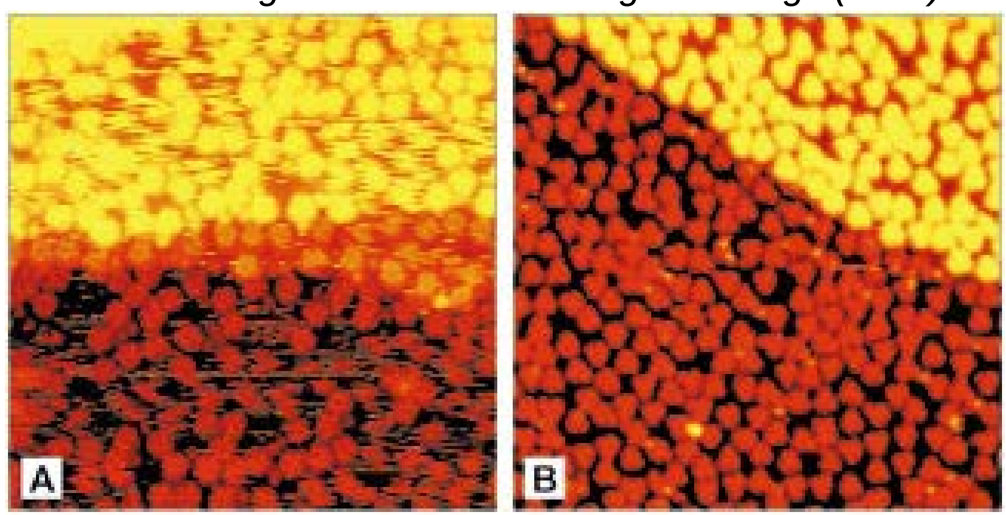


room temperature | *T = 96 K*



close-packed direction

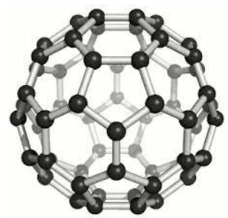
low coverage < 1 ML | *high coverage (1 ML)*

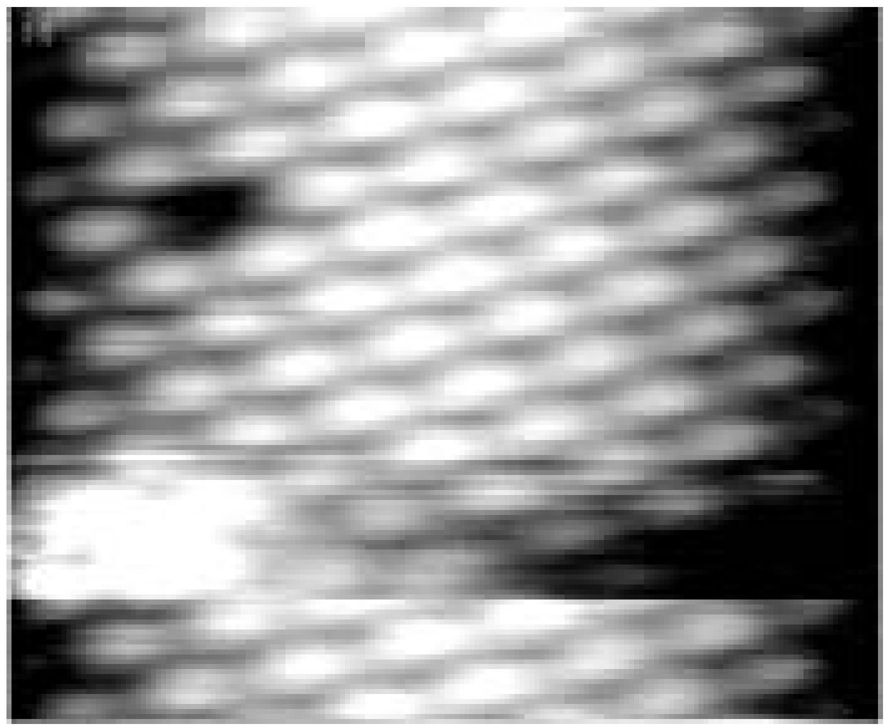


all images: 30 x 30 nm²

M. Schunack et al., J. Chem. Phys. 117, 8493 (2002)

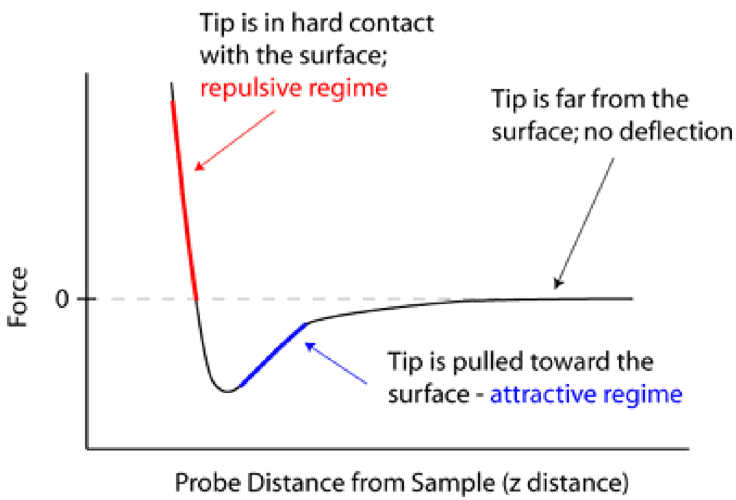
Fullerene C_{60} on the gold surface Au(111)
Imaging at room temperature (real time)

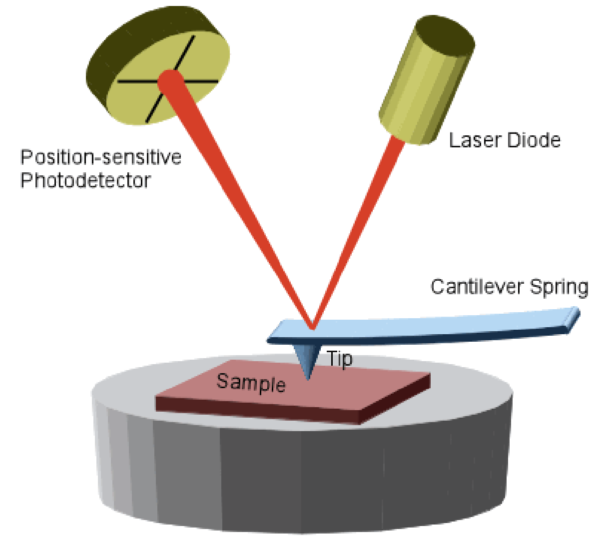


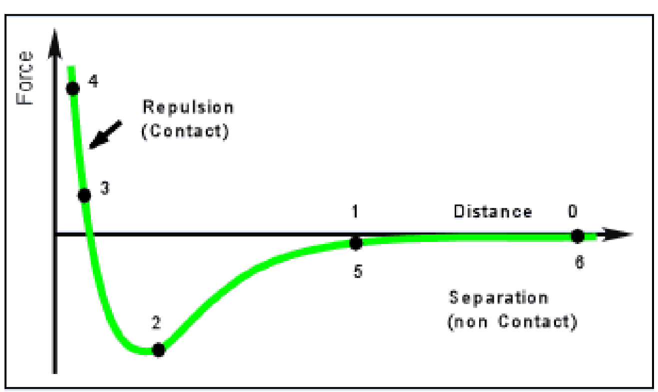


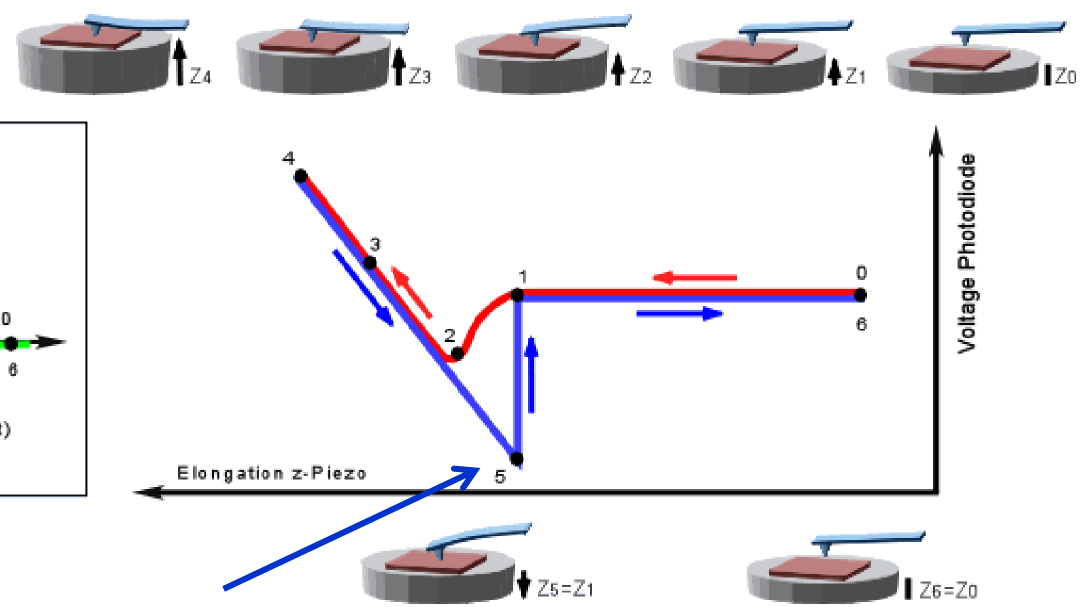
© F. Esch (TU München)

Atomic force microscopy (AFM)



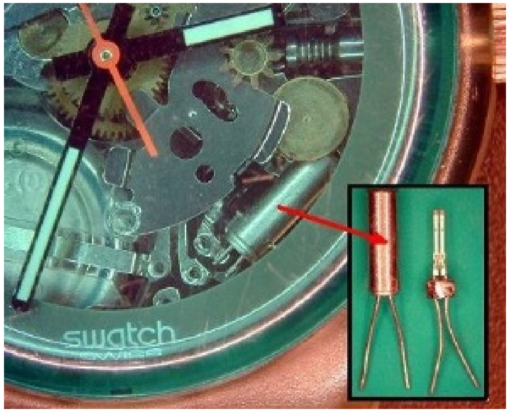


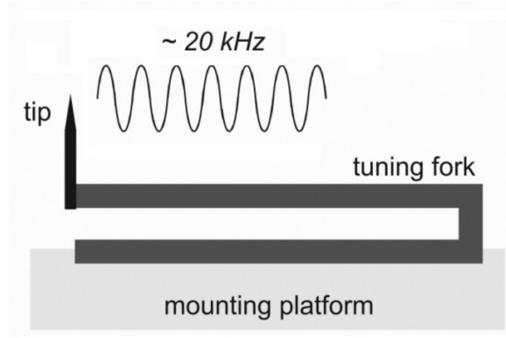




tip sticks in the surface and snaps back

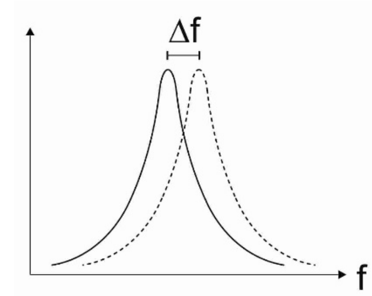
Tuning fork atomic force microscope (AFM)





see F. J. Giessibl, Rev. Mod. Phys. 75, 949 (2003)

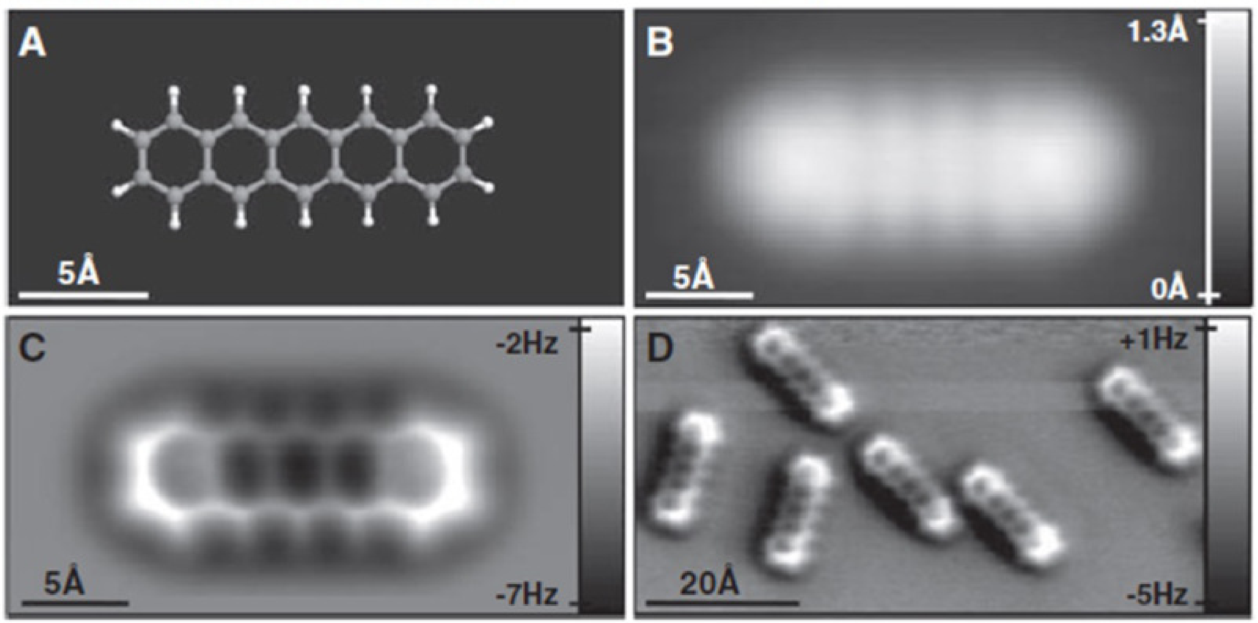
Measurement



Δf is caused by forces between tip and sample

Pentacene: Scanning tunneling "micrograph"

Pentacene molecular model



Pentacene: Atomic force "micrographs"

L. Gross, F. Mohn, N. Moll, P. Liljeroth, and G. Meyer, *Science 325, 1110 (2009)*

IR Spektroskopie

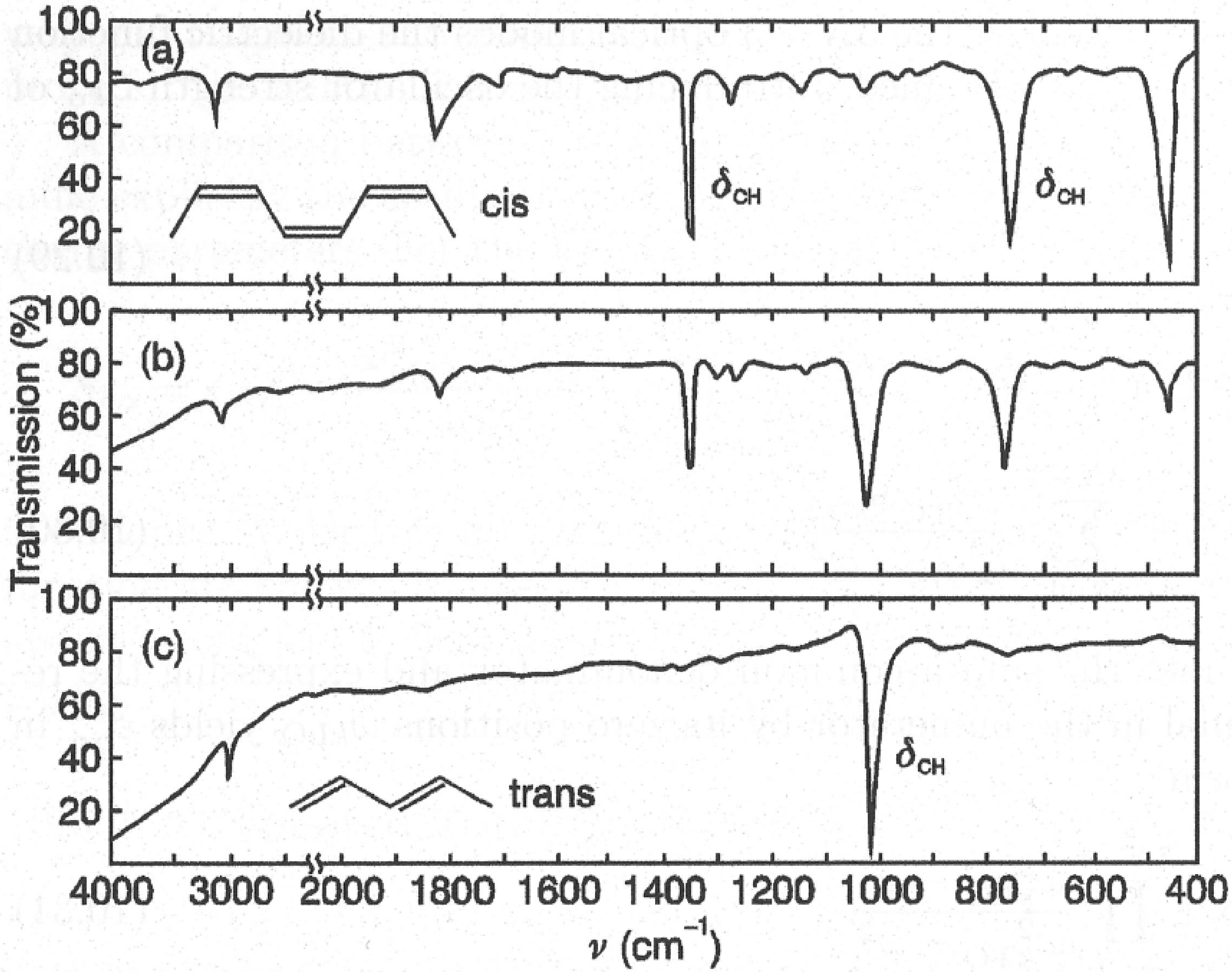
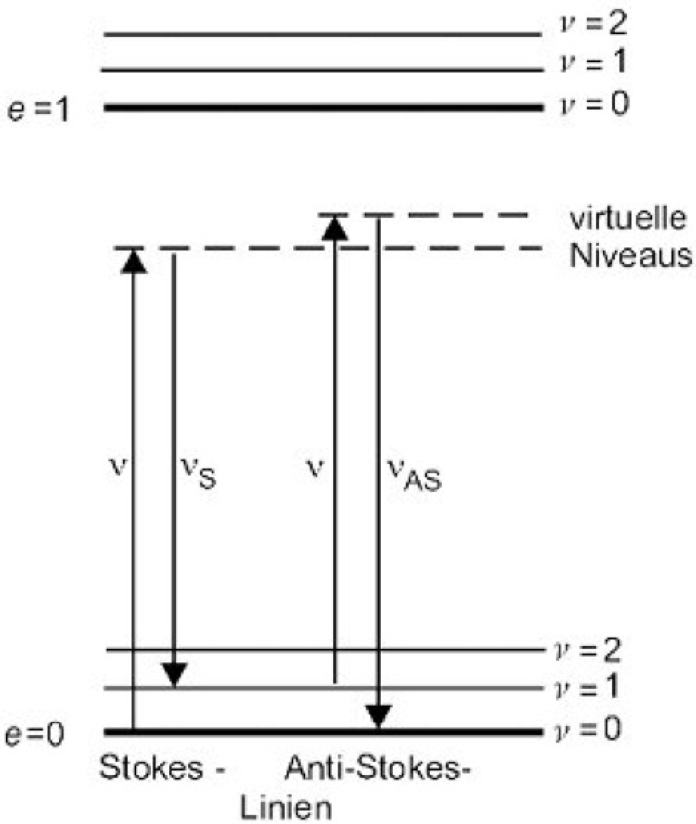
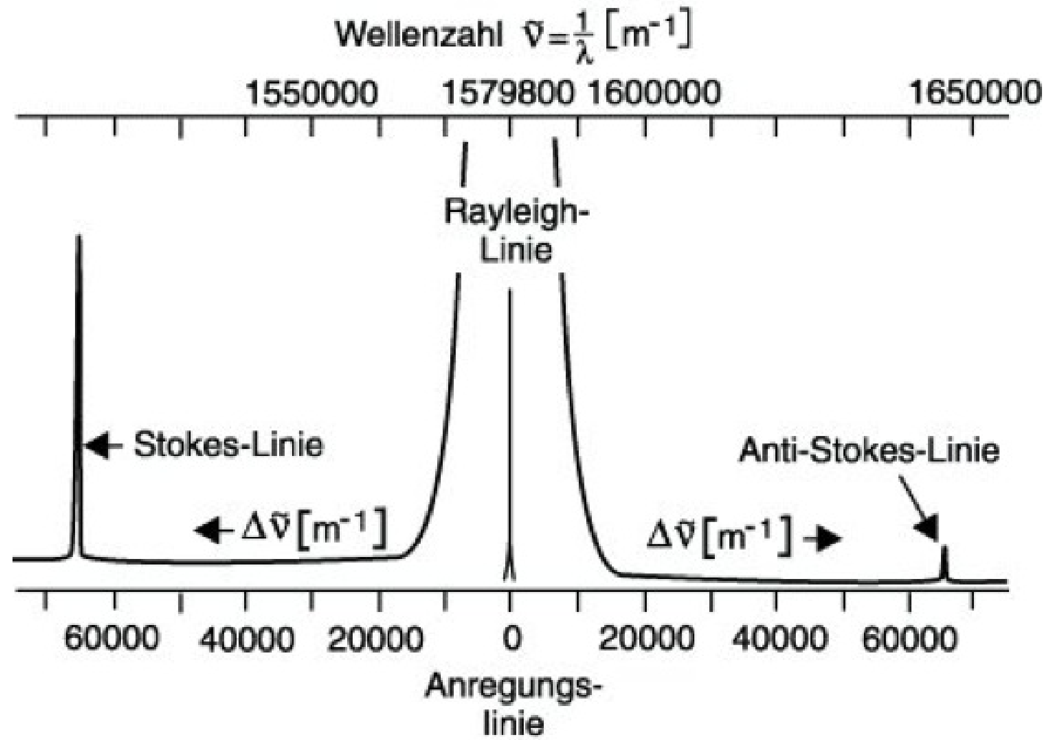


Fig. 10.17. Infrared transmission of cis-polyacetylene during the phase transition into the trans-form. cis-polyacetylene (**a**), intermediate phase (**b**), trans-polyacetylene (**c**); after [10.7]

Kuzmany: Solid-State Spectroscopy, Springer

Raman Spektroskopie





Lexikon der Optik (spektrum.de)

Raman Spektroskopie

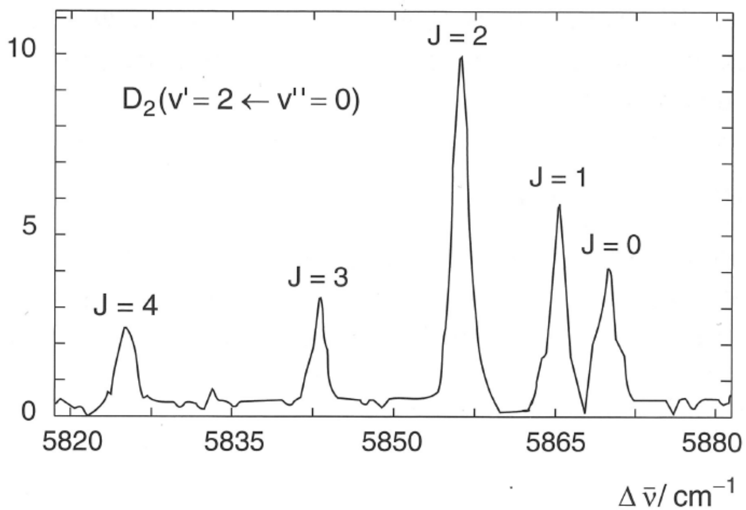


Abb. 10.12. Rotationsaufgelöster Q-Zweig im Oberton-Raman-Spektrum des D_2-Moleküls [10.9]

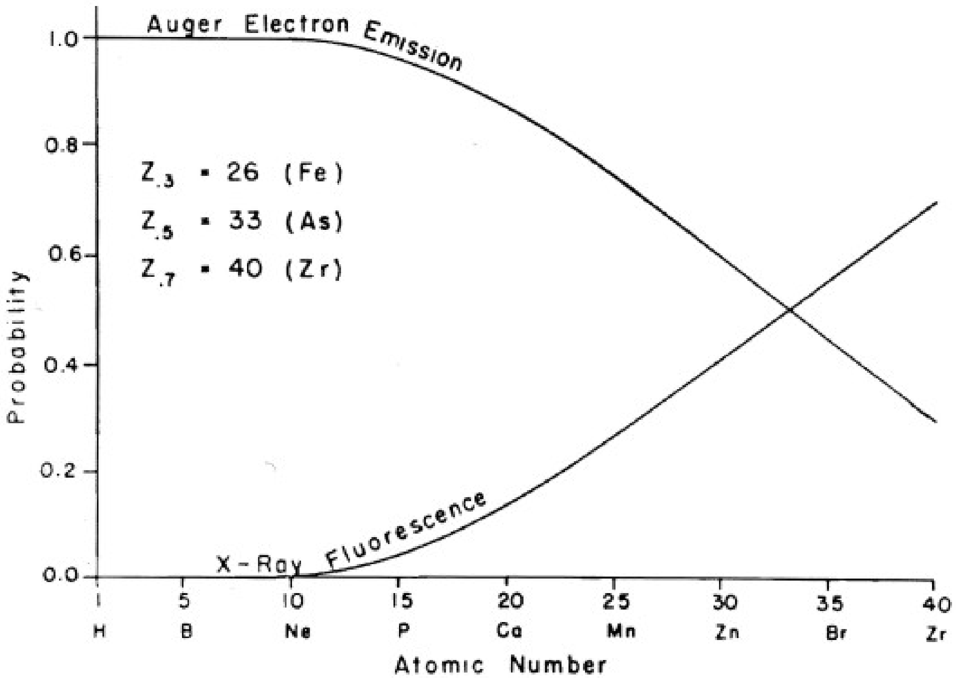
Demtröder: Experimentalphysik 3, Springer

molecule					
vibration					
change of α with Q					
$\frac{d\alpha}{dQ}$	≠0	≠0	≠0	=0	=0
Raman active	yes	yes	yes	no	no
change of $\vec{P}_D$ with Q					
$\frac{d\vec{P}_D}{dQ}$	=0	≠0	=0	≠0	≠0
infrared active	no	yes	no	yes	yes

Fig. 9.4. Selection rules for Raman and for infrared activity of vibrations;

Kuzmany: Solid-State Spectroscopy, Springer

Auger Electron Spectroscopy (AES)



Briggs/Seah, Practical Surface Analysis Vol.1 (Wiley)

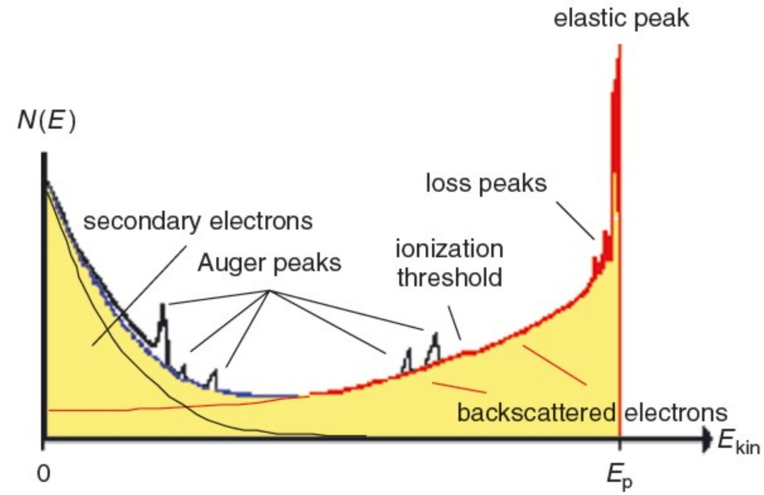


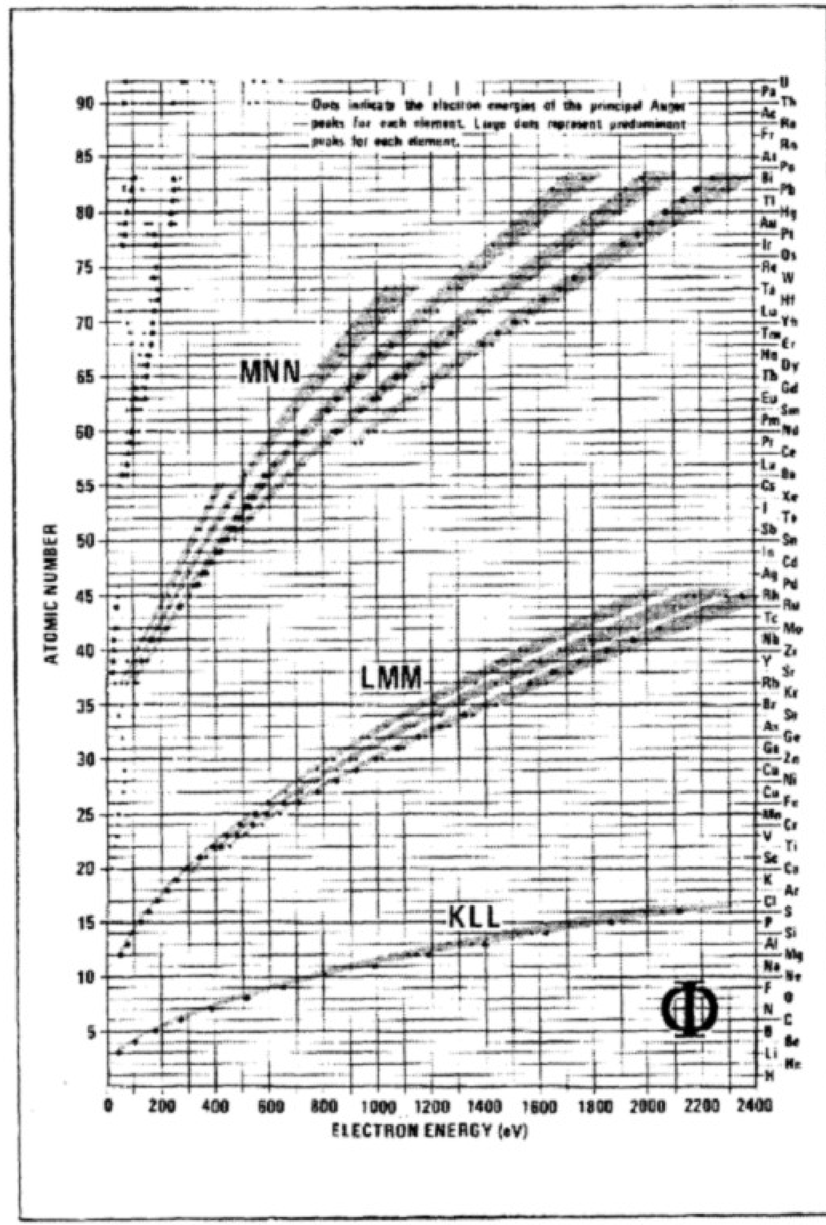
Figure 2.3 Schematic representation of an Auger spectrum

Surface Analysis – The Principal Techniques, Wiley (2009)

AES

Quantum numbers			X-ray suffix	X-ray level	Spectroscopic level
n	l	j			
1	0	$\frac{1}{2}$	1	K	$1s_{1/2}$
2	0	$\frac{1}{2}$	1	L_1	$2s_{1/2}$
2	1	$\frac{1}{2}$	2	L_2	$2p_{1/2}$
2	1	$\frac{3}{2}$	3	L_3	$2p_{3/2}$
3	0	$\frac{1}{2}$	1	M_1	$3s_{1/2}$
3	1	$\frac{1}{2}$	2	M_2	$3p_{1/2}$
3	1	$\frac{3}{2}$	3	M_3	$3p_{3/2}$
3	2	$\frac{3}{2}$	4	M_4	$3d_{3/2}$
3	2	$\frac{5}{2}$	5	M_5	$3d_{5/2}$
	etc.		etc.	etc.	etc.

Briggs/Seah, Practical Surface Analysis Vol.1 (Wiley)



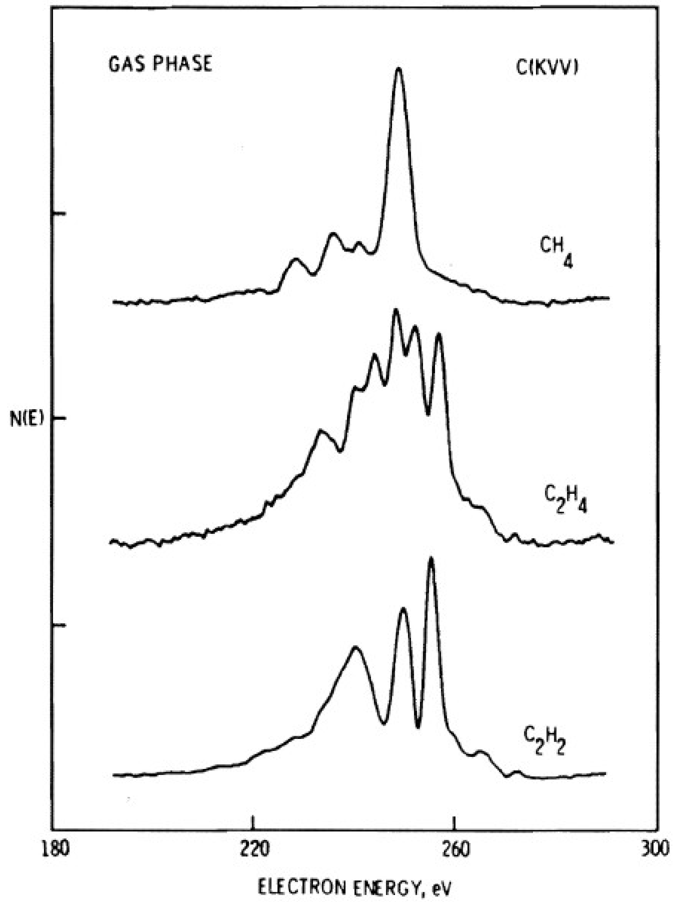
Handbook of Auger Electron Spectroscopy (1978)

Electron binding energies (in eV)

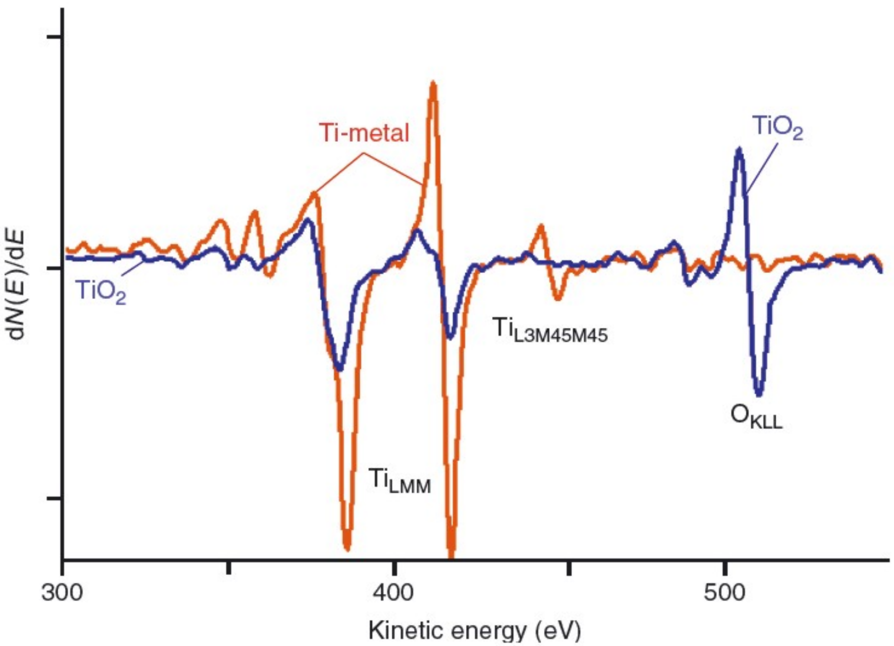
Z	EL	K	L1	L2	L3	M1	M2	M3	M4	M5
1	H	13.6								
2	HE	24.6								
3	LI	54.8	5.3							
4	BE	112.1	8.0							
5	B	188.0	12.6	4.7	4.7					
6	C	283.8	18.0	6.4	6.4					
7	N	401.6	24.4	9.2	9.2					
8	O	532.0	28.5	7.1	7.1					
9	F	685.4	34.0	8.6	8.6					
10	NE	870.1	48.5	21.7	21.6					
11	NA	1072.1	63.3	31.1	31.1	0.7				
12	MG	1305.0	89.4	51.4	51.4	2.1				
13	AL	1559.6	117.7	73.2	72.7	0.7	5.5	5.5		
14	SI	1838.9	148.7	99.5	98.9	7.6	3.0	3.0		
15	P	2145.5	189.3	136.2	135.3	16.2	9.9	9.9		
16	S	2472.0	229.2	165.4	164.2	15.8	8.0	8.0		
17	CL	2822.4	270.2	201.6	200.0	17.5	6.8	6.8		
18	AR	3206.0	326.3	250.7	248.6	29.2	15.9	15.8		
19	K	3607.4	377.1	296.3	293.6	33.9	17.8	17.8		
20	CA	4038.1	437.8	350.0	346.4	43.7	25.4	25.4		
21	SC	4492.8	500.4	406.7	402.2	53.8	32.3	32.3	6.6	6.6
22	TI	4966.4	563.7	461.5	455.5	60.3	34.6	34.6	3.7	3.7
23	V	5465.1	628.2	520.5	512.9	66.5	37.8	37.8	2.2	2.2
24	CR	5989.2	694.6	583.7	574.5	74.1	42.5	42.5	2.3	2.3
25	MN	6539.0	769.0	651.4	640.3	83.9	48.6	48.6	3.3	3.3
26	FE	7112.0	846.1	721.1	708.1	92.9	54.0	54.0	3.6	3.6
27	CO	7708.9	925.6	793.6	778.6	100.7	59.5	59.5	2.9	2.9
28	NI	8332.8	1008.1	871.9	854.7	111.0	68.1	68.1	3.6	3.6
29	CU	8978.9	1096.1	951.0	931.1	119.8	73.6	73.6	1.6	1.6
30	ZN	9658.6	1193.6	1042.8	1019.7	135.9	86.6	86.6	8.1	8.1

Atom. Data Nucl. Data Tables 20, 311 (1977)

Auger chemical fine structure



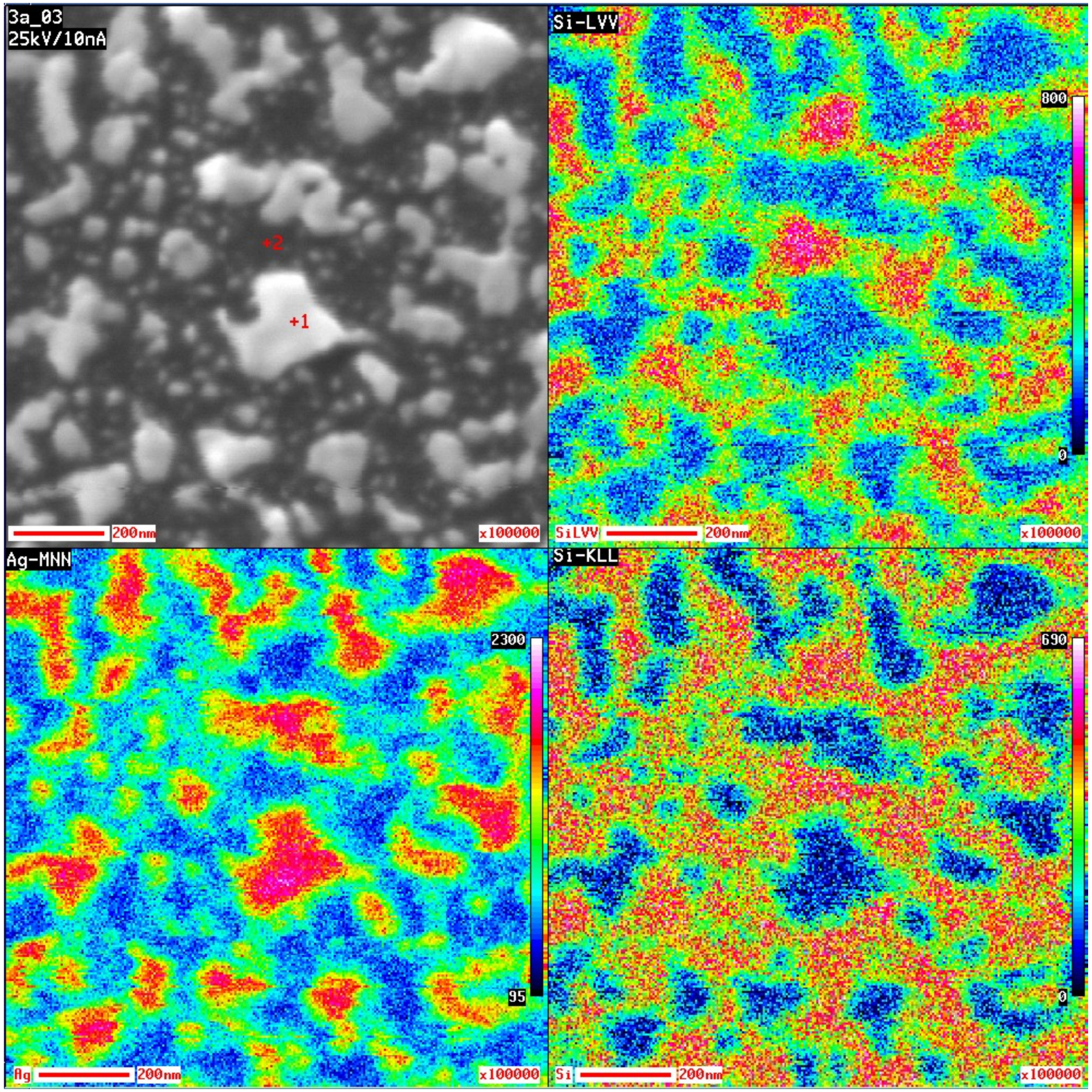
Briggs/Seah, Practical Surface Analysis Vol.1 (Wiley)



Surface Analysis – The Principal Techniques, Wiley (2009)

Scanning Auger Microscopy (SAM)

Ag clusters on a Si surface



Alberta Centre for Surface Engineering and Science (ACSES)

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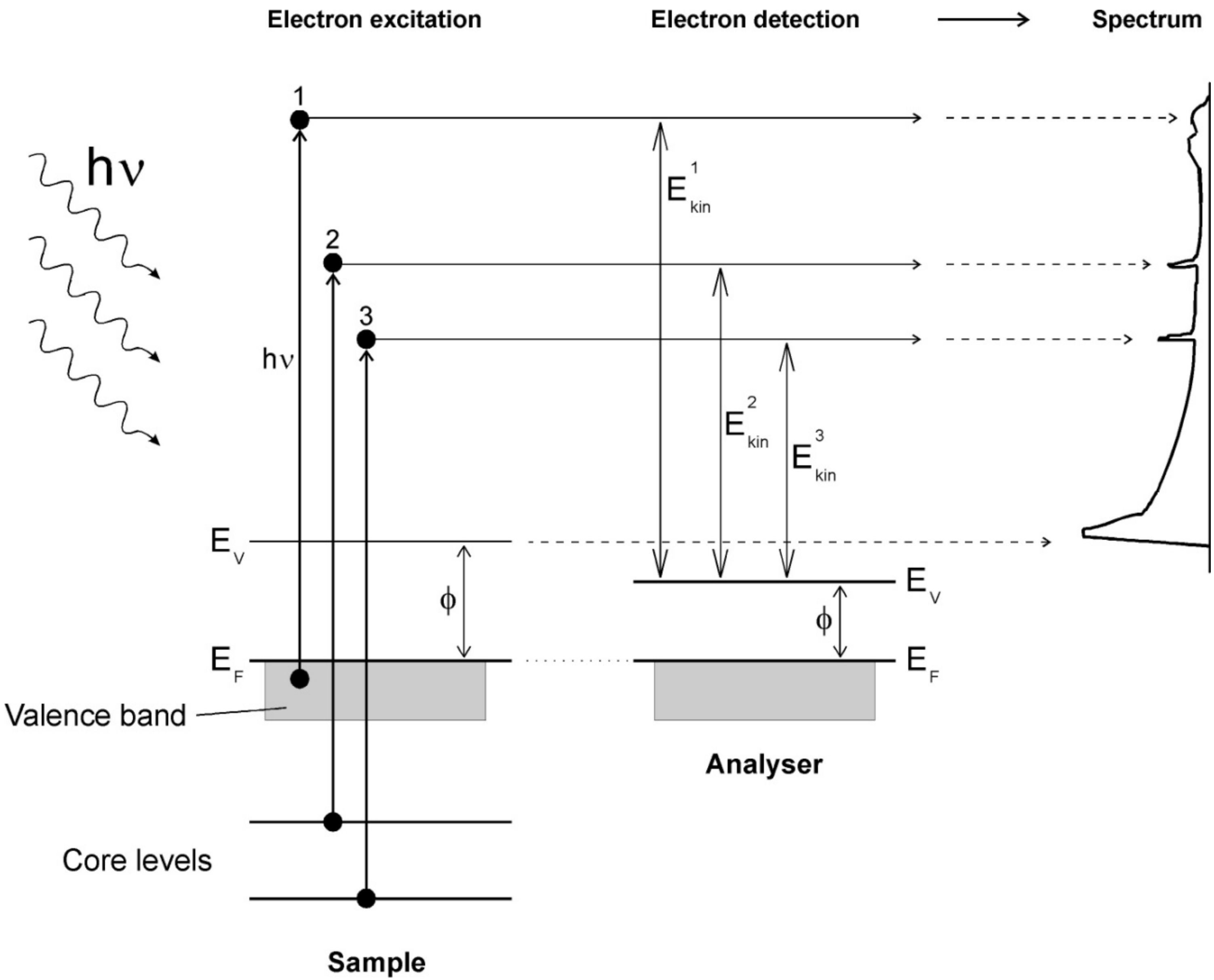
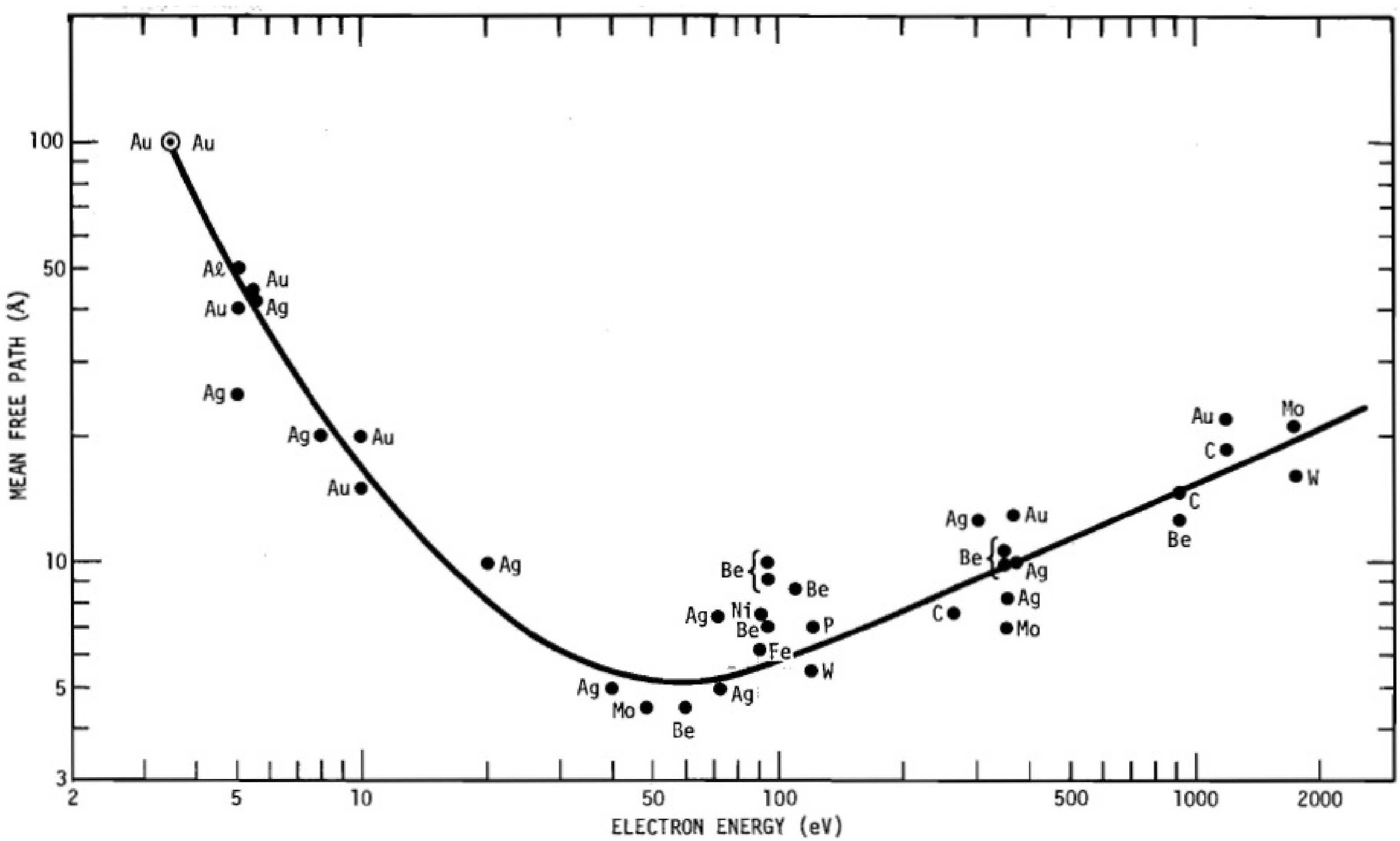


Elektronenweglänge in Festkörpern: „Universal curve“



G. A. Somorjai, Chemistry in two dimensions: Surfaces

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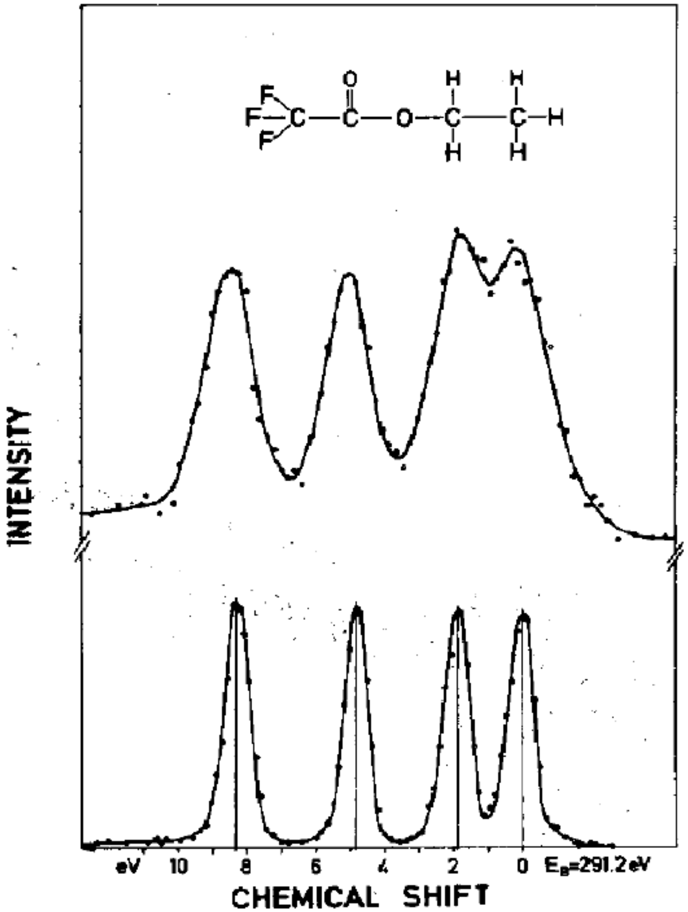

Fig. 28. The ESCA shifts of the C 1s in ethyl trifluoroacetate.
Upper spectrum without and lower with monochromatization.

K. Siegbahn, J. El. Spectr. Rel. Phen. 5, 3 (1974)

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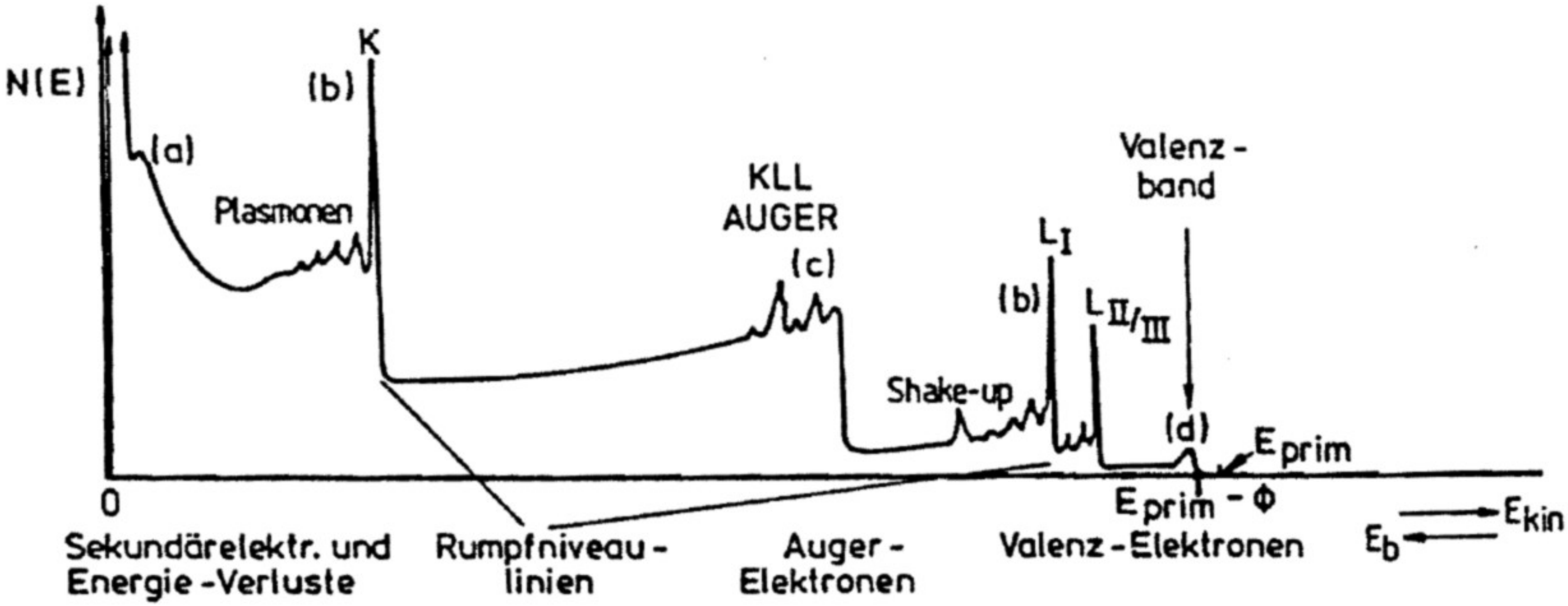

Henzler/Göpel: Oberflächenphysik des Festkörpers, Teubner

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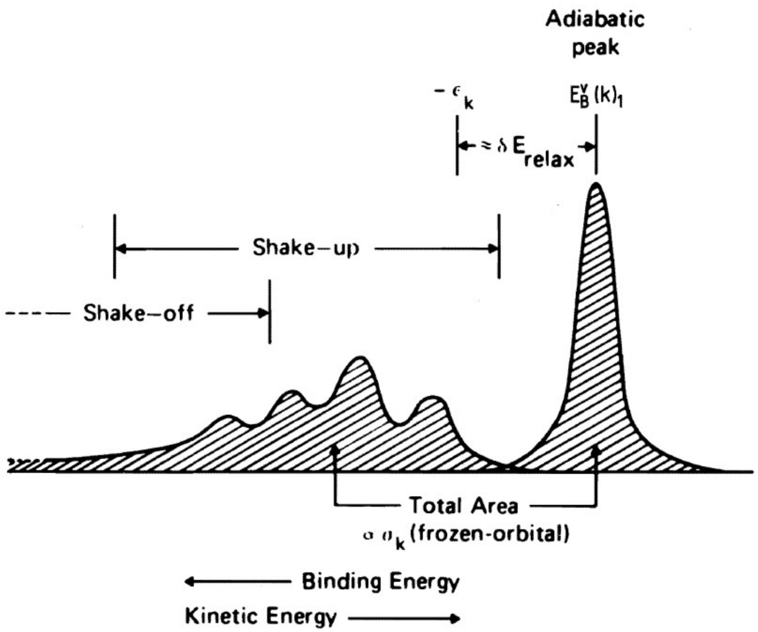
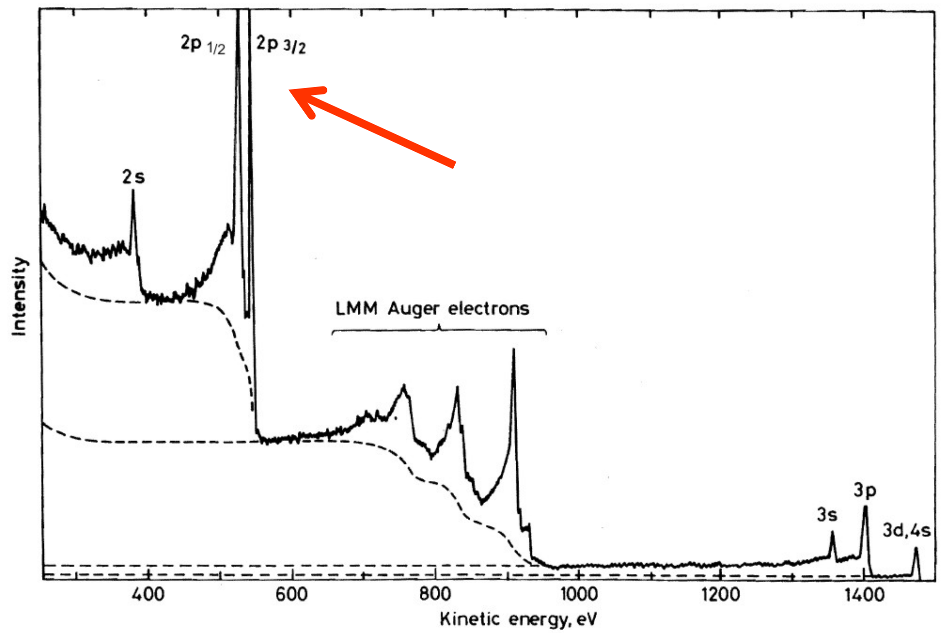


Ertl/Küppers, Low energy electrons and surface chemistry, VCH

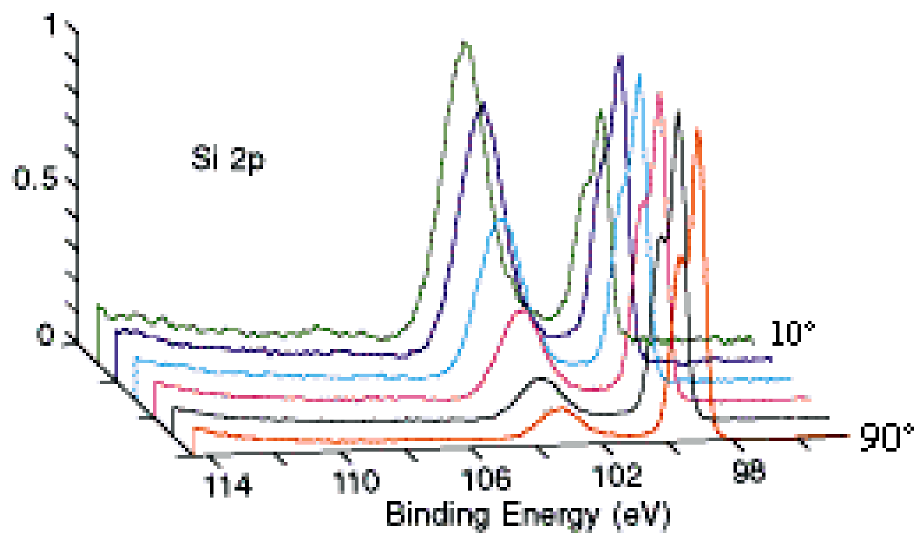


Briggs/Seah, Practical Surface Analysis Vol.1 (Wiley)

Angle dependence

Si sample covered with an oxide layer

Si 2p for different emission angles



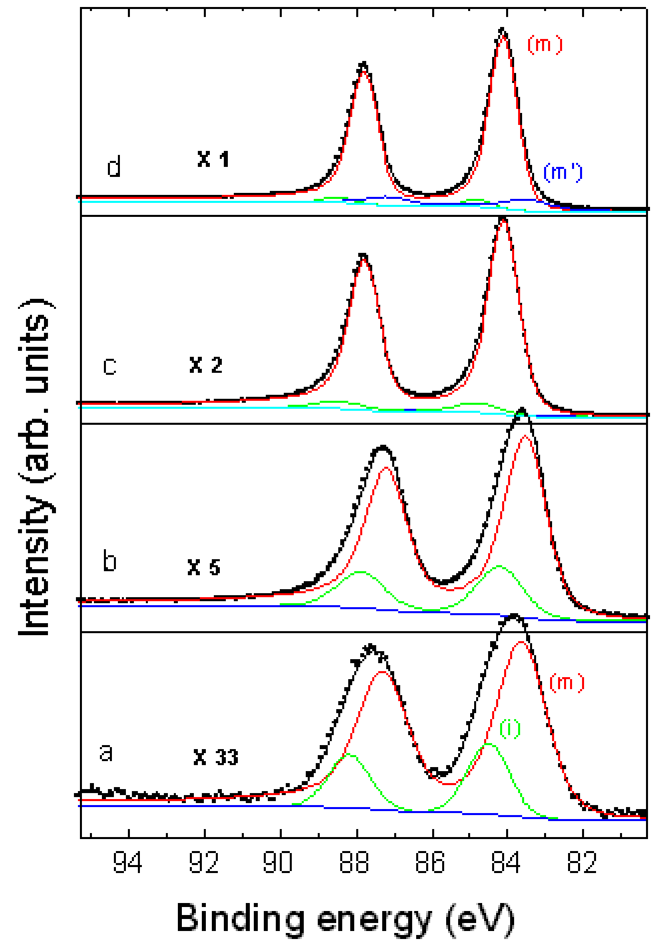
Physical Electronics, Inc. (PHI)

Si peak of the oxide at 103 eV changes…

Fitting

Au on GaN (Au 4f peaks)

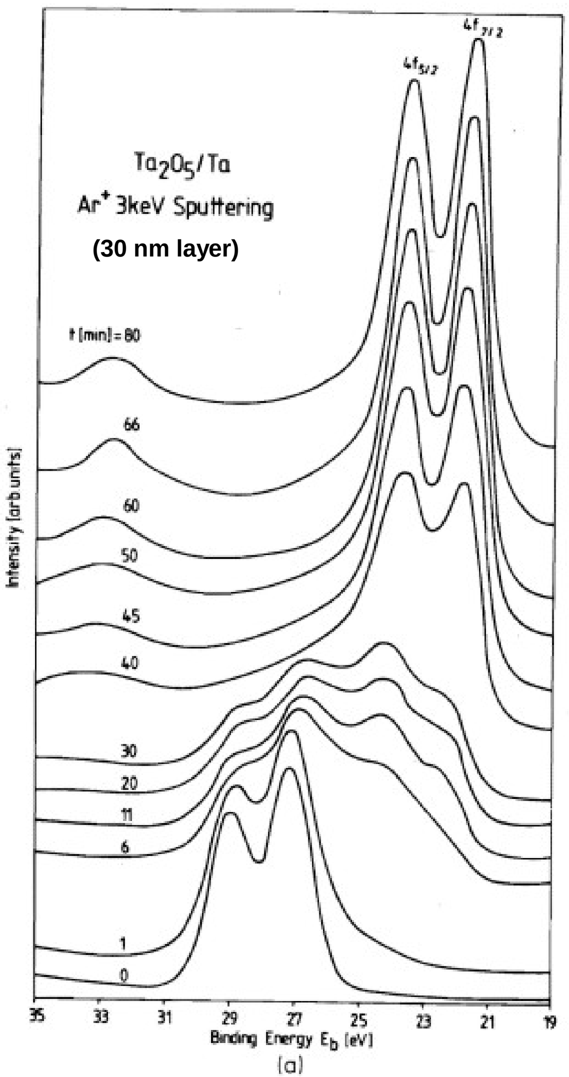
Increasing Au coverage (from a to d)

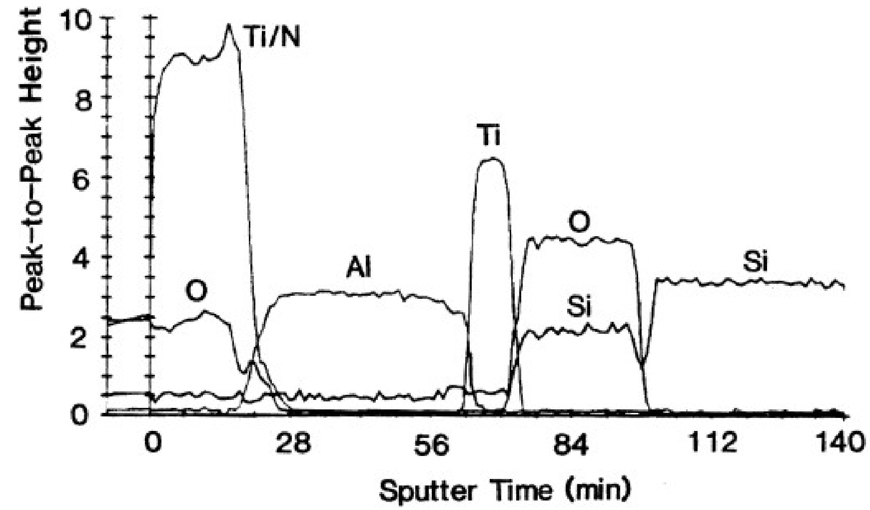


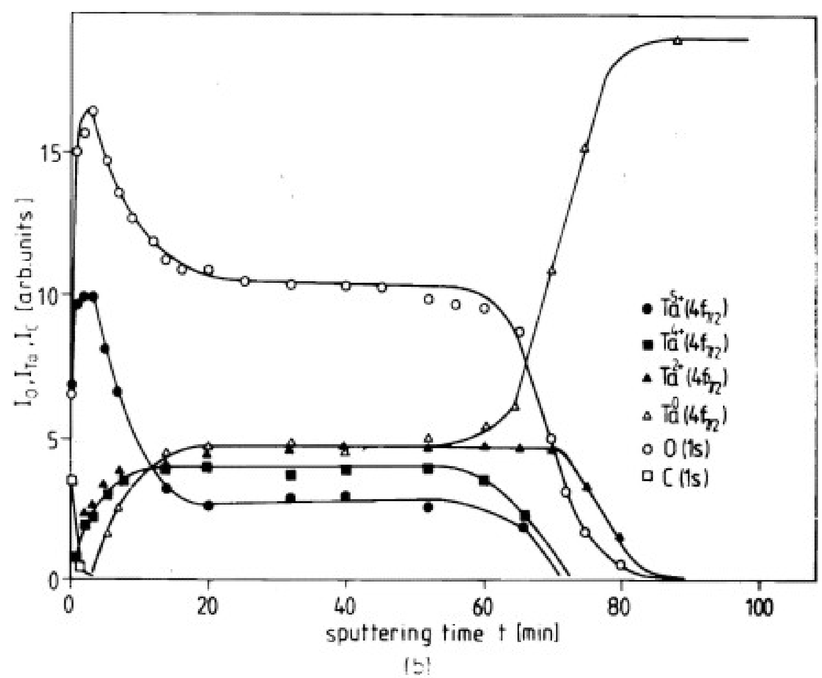
R. Sporken et al.

Depth profiling

Sputtering during AES analysis





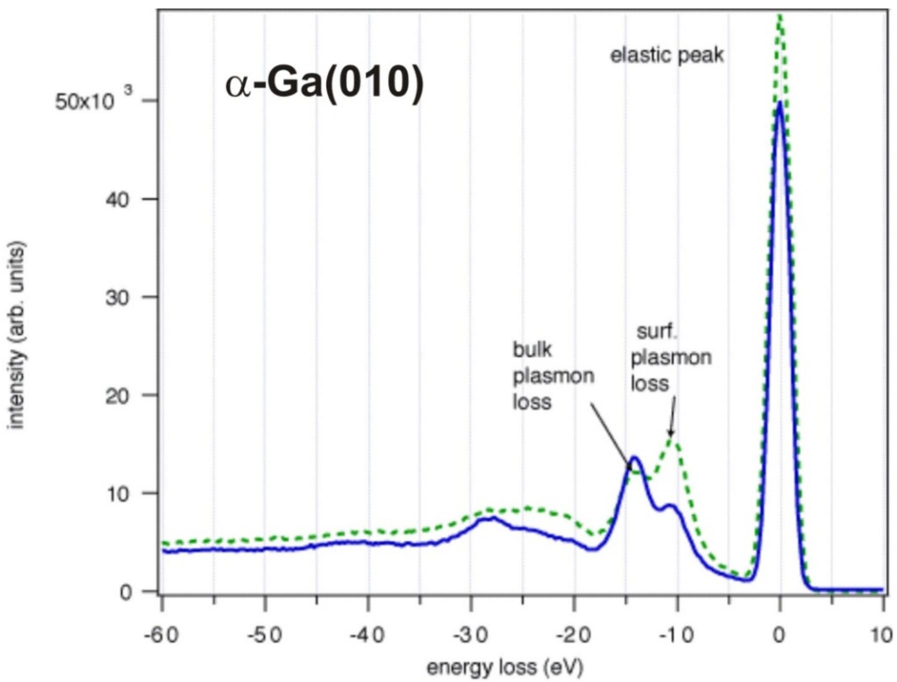


Briggs/Seah, Practical Surface Analysis, Wiley

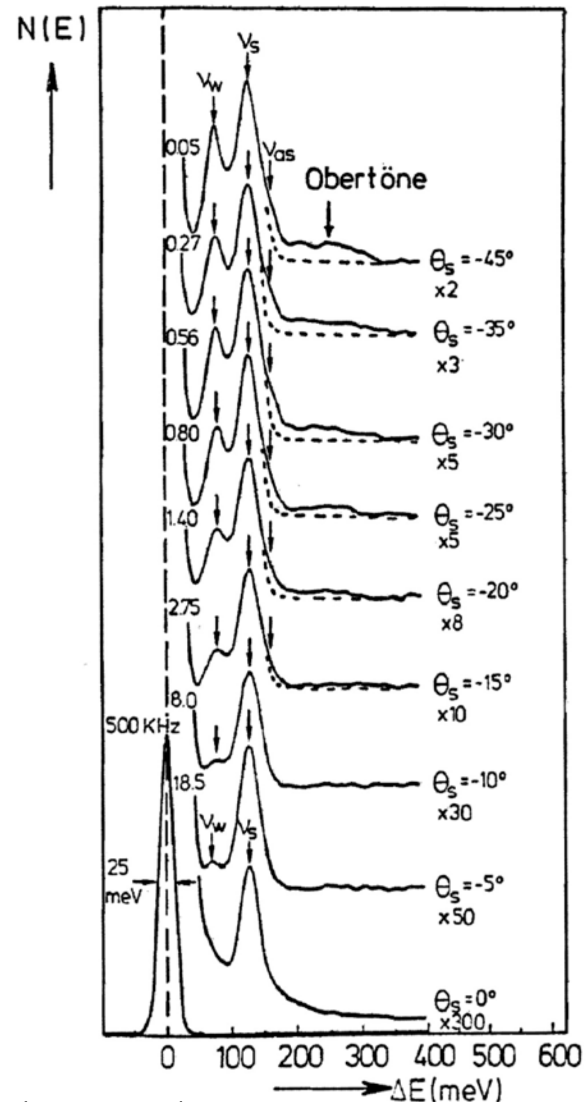
EELS

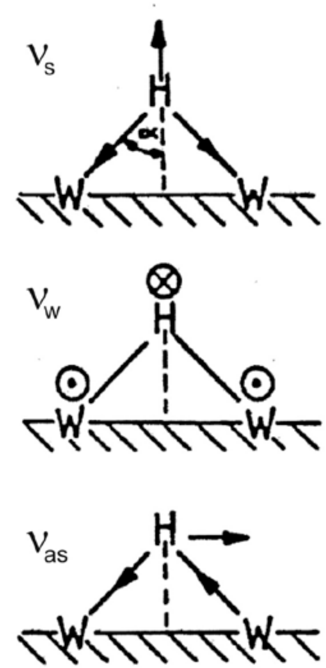
H on W(100)

Different geometries



P. Hofmann (Univ. Aarhus)





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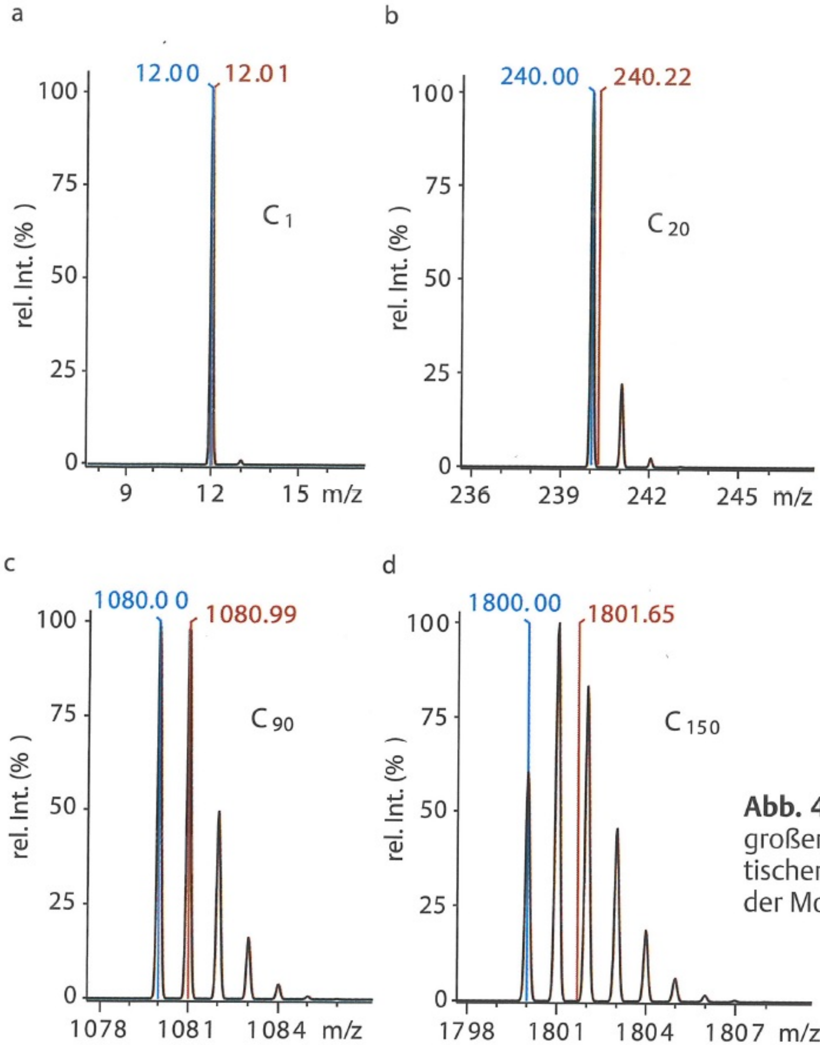
Tab. 4.1 Atommassen einiger wichtiger Elemente, deren natürliche Isotope mit natürlicher Häufigkeit und exakten Massen, sowie Klassifizierung[1]

Element	Atommasse	nominale Masse	Isotopen	rel. Häufigkeit (%)	isotopische Massen	Klassifizierung
H	1.00794	1	^{1}H	99.985	1.007825	X
			^{2}H = D	0.015	2.0141102	**X + 1**
Li	6.941	7	^{6}Li	7.5	6.015123	**X – 1**
			^{7}Li	92.5	7.016005	X
B	10.811	11	^{10}B	19.9	10.012938	**X – 1**
			^{11}B	80.1	11.009305	X
C	12.011	12	^{12}C	98.90	12.000000	X
			^{13}C	1.10	13.003355	**X + 1**
N	14.00674	14	^{14}N	99.634	14.003074	X
			^{15}N	0.366	15.000109	**X + 1**
O	15.9994	16	^{16}O	99.762	15.994915	X
			^{17}O	0.038	16.999131	X + 1
			^{18}O	0.200	17.999159	**X + 2**
F	18.998403	19	^{19}F	100	18.998403	X
Na	22.989768	23	^{23}Na	100	22.989770	X
Si	28.0855	28	^{28}Si	92.23	27.976928	X
			^{29}Si	4.67	28.976496	X + 1
			^{30}Si	3.10	29.973772	**X + 2**
P	30.973762	31	^{31}P	100	30.973763	X
S	32.066	32	^{32}S	95.02	31.972072	X
			^{33}S	0.75	32.971459	X + 1
			^{34}S	4.21	33.967868	**X + 2**
			^{35}S	0.02	35.967079	X + 3
Cl	35.4527	35	^{35}Cl	75.77	34.968853	X
			^{37}Cl	24.23	36.965903	**X + 2**
Ar	39.948	40	^{36}Ar	0.337	35.967546	X – 4
			^{38}Ar	0.063	37.962732	X – 2
			^{40}Ar	99.600	39.962383	X
Fe	55.847	56	^{54}Fe	5.8	53.939612	**X – 2**
			^{56}Fe	91.72	55.934939	X
			^{57}Fe	2.2	56.935396	X + 1
			^{58}Fe	0.28	57.933278	X + 2

Source: Spektroskopische Methoden in der organischen Chemie, Hesse/Meier/Zeeh



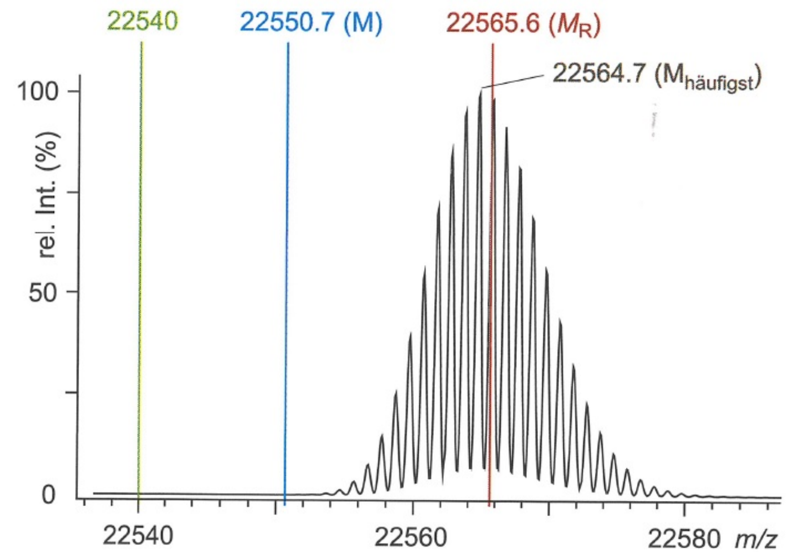


Abb. 4.9 Berechnete Isotopenverteilung für das Ion eines hypothetischen Biopolymers (Peptid) mit der Summenformel $C_{1000}H_{1500}N_{280}O_{290}S_{15}$ (blau: monoisotopische Masse (M), rot: Molmasse (M_R) die ungefähr der häufigsten Masse ($M_{häufigst}$) entspricht, grün: Nominalmasse

Abb. 4.8 Einfluss der Anzahl C-Atome auf die Isotopenverteilung bei großen Molekülen anhand der berechneten $M^{+\bullet}$ Spektren hypothetischer C_n-Verbindungen (blau: monoisotopische Masse, rot: Lage der Molmasse (M_R))

Source: Spektroskopische Methoden in der organischen Chemie, Hesse/Meier/Zeeh

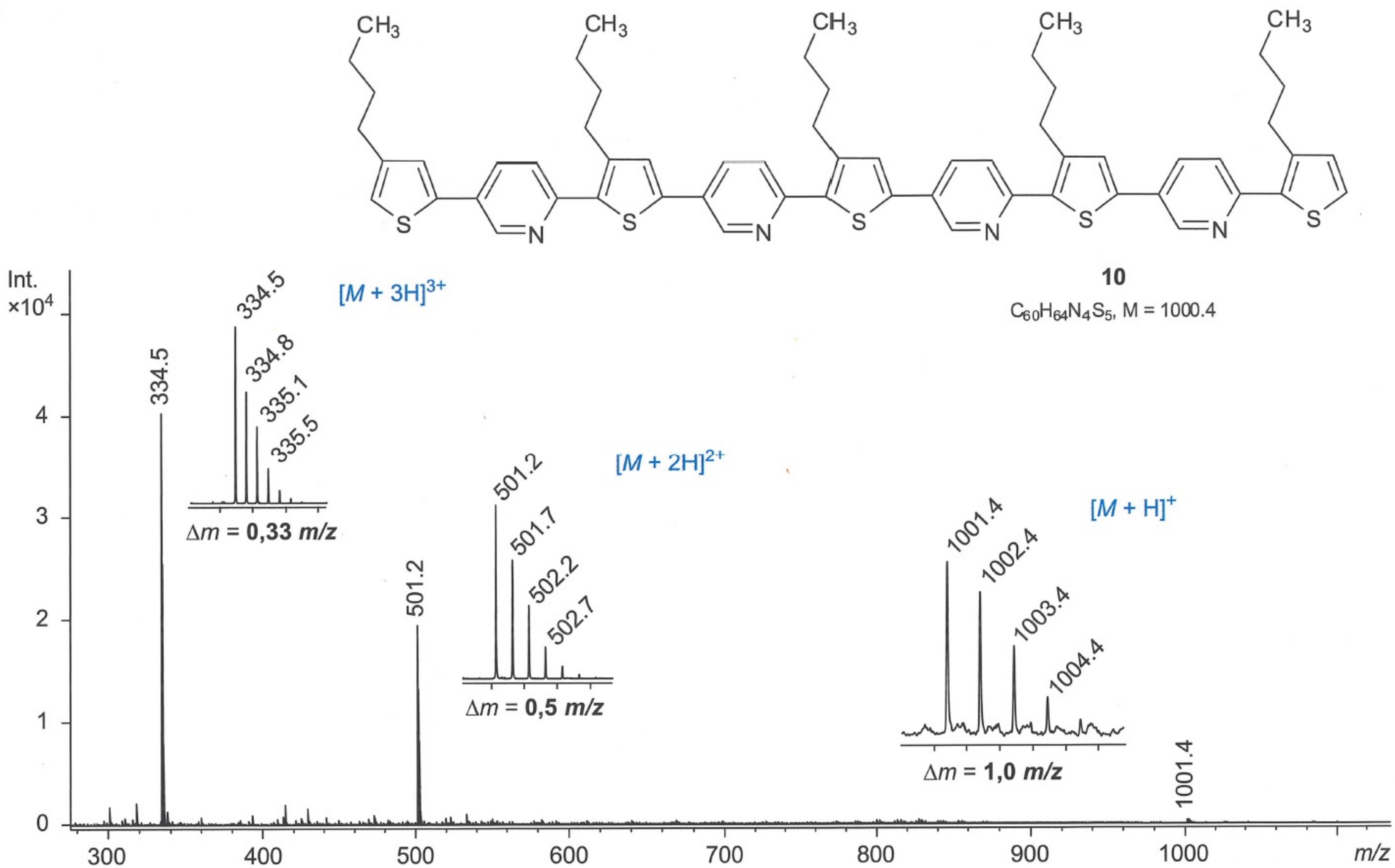


Abb. 4.10 ESI-MS der Verbindung **10** mit Signalen für Ionen des Typs $[M + H]^{+}$, $[M + 2H]^{2+}$ und $[M + 3H]^{3+}$ (Probe von N. Finney, Universität Zürich)

Source: Spektroskopische Methoden in der organischen Chemie, Hesse/Meier/Zeeh

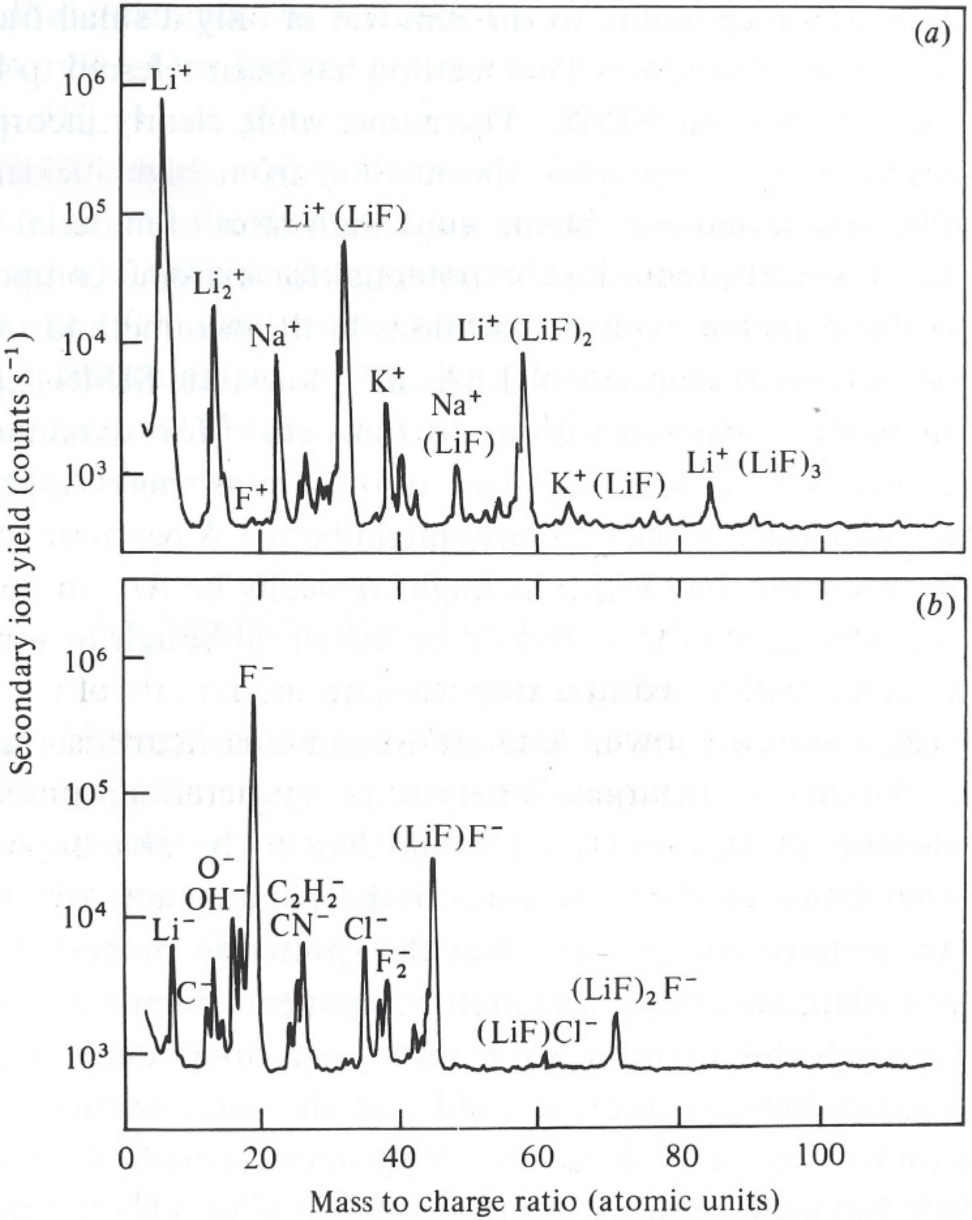


Fig. 4.47 Positive (*a*) and negative (*b*) SIMS spectra from a LiF{100} surface using 1.3 keV Ar^+ ions incident at 60° (after Estel *et al.*, 1976).

Source: Modern Techniques of Surface Science, 2nd edition
Woodruff & Delchar