Trends in the Adsorption Behaviour of the Heaviest Element

V. Pershina

GSI, Darmstadt

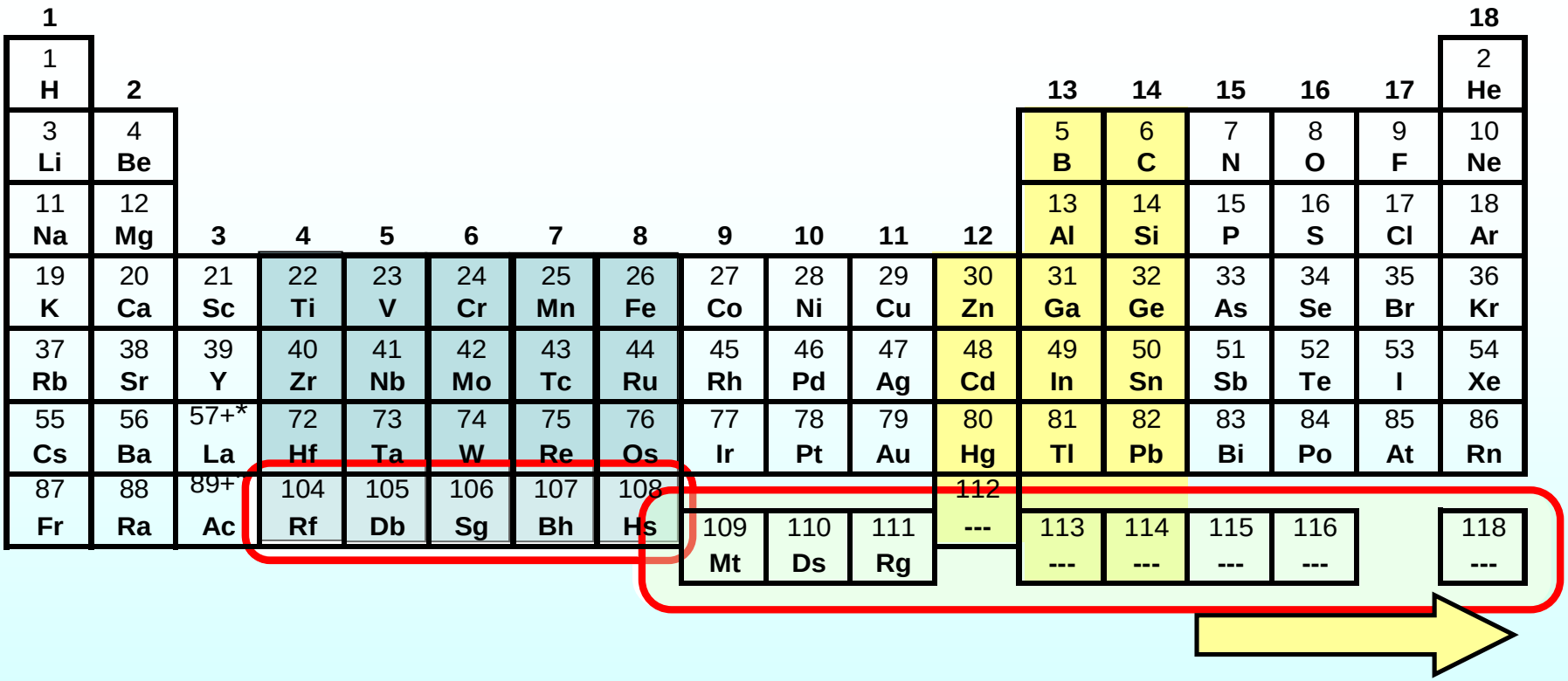
J. Anton and T. Jacob

University of Ulm

A. Borschevsky, E. Eliav and U. Kaldor

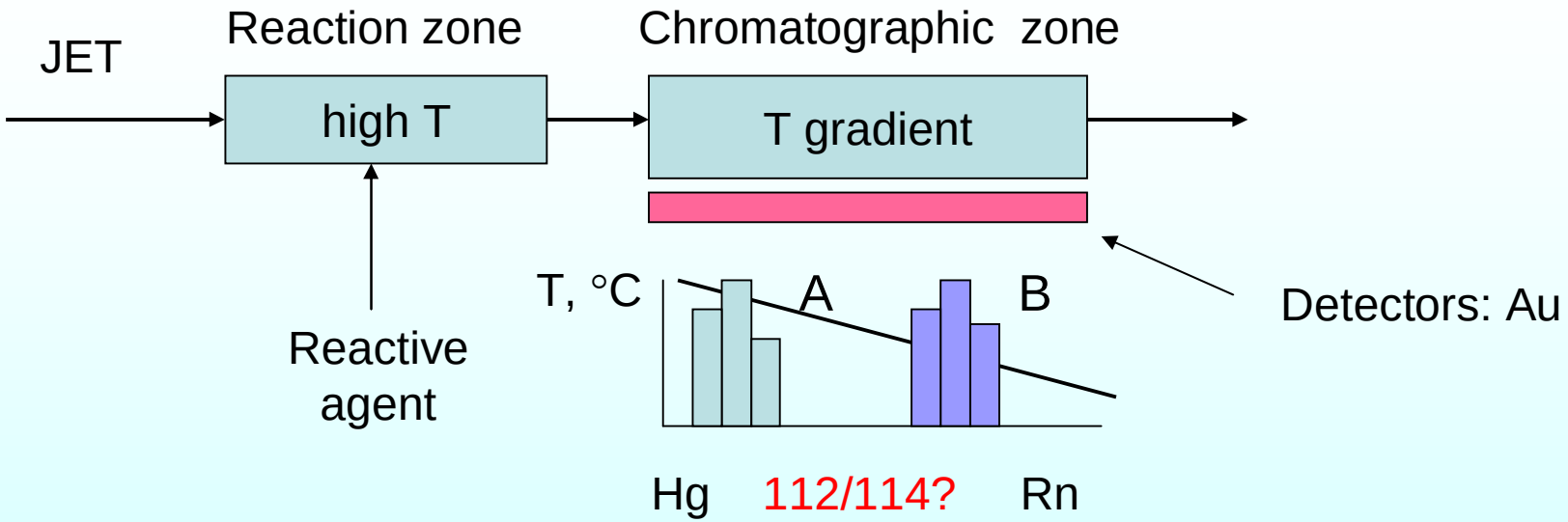
Tel Aviv University

Periodic Systems of Elements



Gas-Phase Chromatography
Experiments with Atoms and Molecules

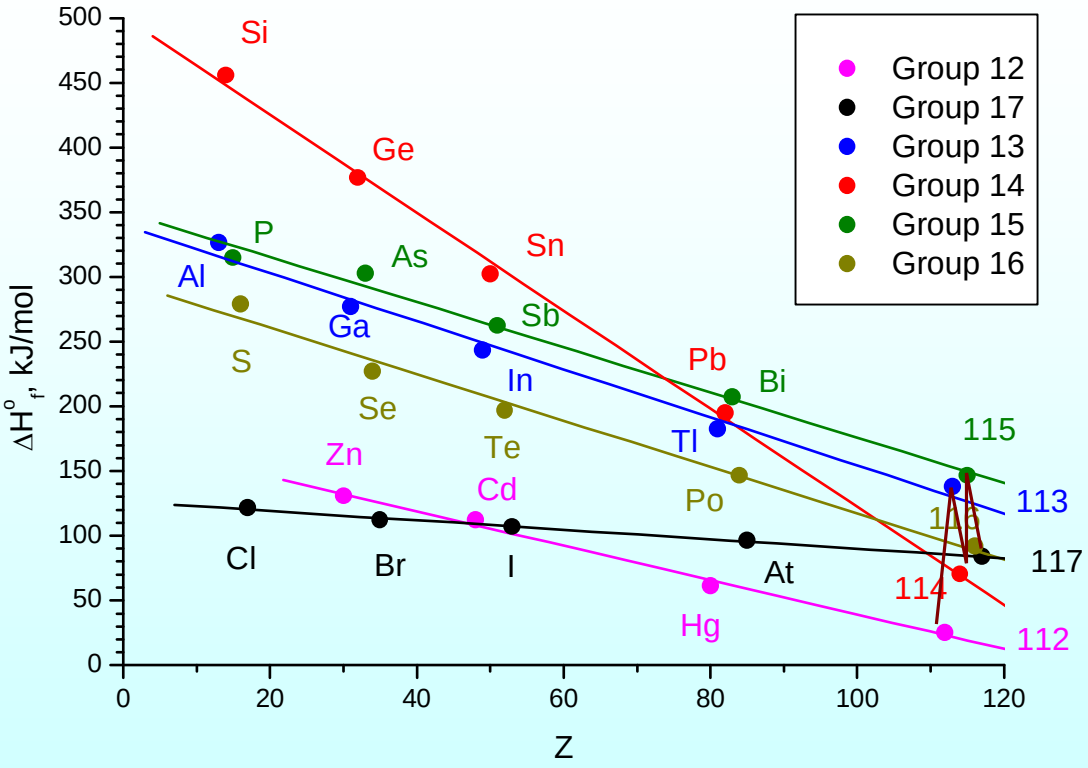
Isothermal Chromatography



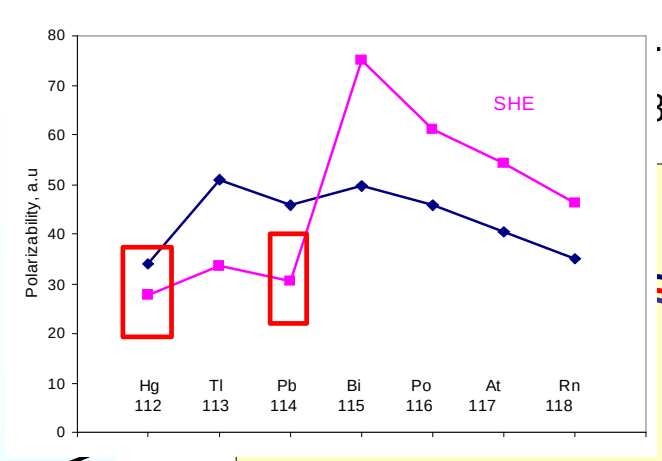
Measured: $T_{ads} \xrightarrow{\text{models'}} \Delta H_{ads} \xrightarrow{\sim} \Delta H_{sub}$

Calculated: $\Delta H_{a} \neq T_{ads}$ (ideal surfaces!)

Formation Enthalpies of Group 12-17 Elements (ΔH_{sub} of Metals)

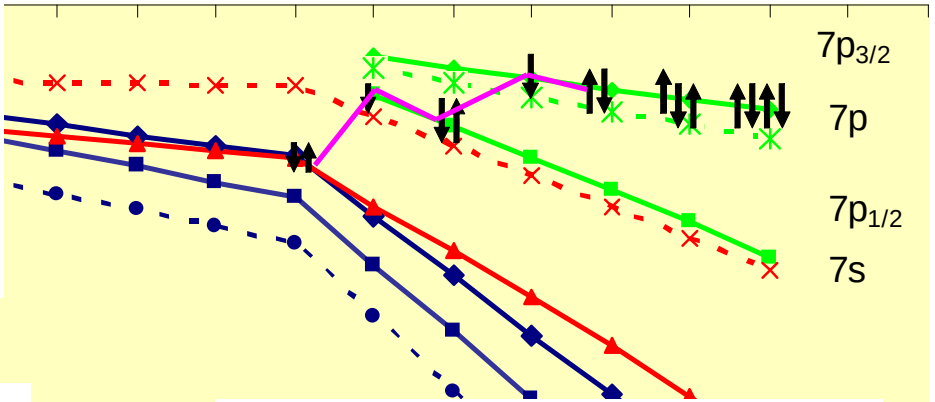


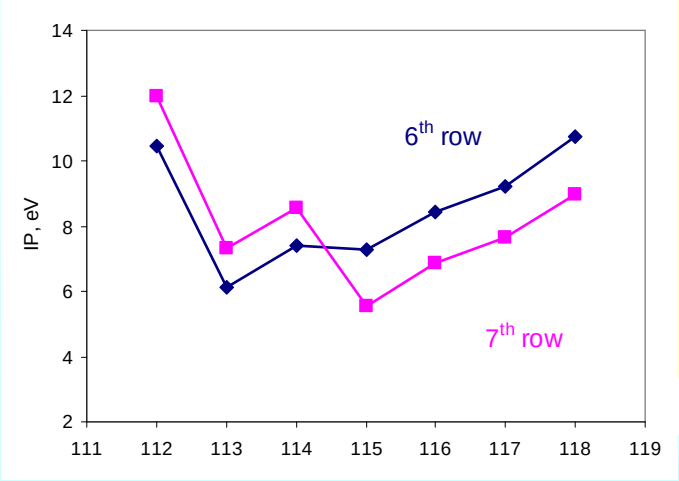
Relativistic Dirac-Fock and Nonrelativistic Energies of the Valence Orbitals (eV)

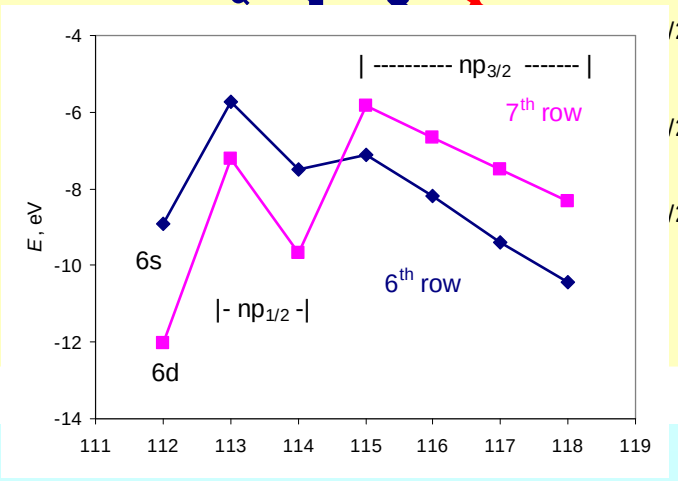


$d^{10}s^2$ $s^2p_{1/2}^1$ $s^2p_{1/2}^2$ ..... s^2p^6

109 110 111 112 113 114 115 116 117 118 119 120







Quantum-Chemical Methods

- DC(B) *ab initio* + CCSD(T)

Nastya

  - Atoms, small molecules
    - 112, 114, HgAu
  - Larger molecules
    - SgO_2Cl_2, $114F_4$

- Effective Core Potentials (2*c*-ECP)
  - Relativistic ECP (RECP) + CCSD(T)
  - Pseudo-Potentials (PP) + CCSD(T)

- 4*c*-Density-Functional Theory
  - 4*c*-DFT (E^{xc} = B88/P86, etc.)
  - 4*c*-BDF

- Other

Josef

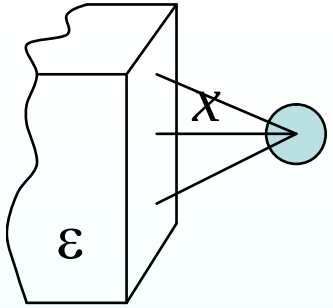
  - Molecules, complexes, clusters, solid state
    - SgO_2Cl_2, 112-Au_n, $SgO_n(H_2O)_mL_y^{q-}$, etc.

Adsorption on Inert Surfaces

For weak interactions:

Atom-slab model:

$$E(x) = -\frac{3}{16}\left(\frac{\varepsilon - 1}{\varepsilon + 2}\right)\frac{\alpha_{at}}{\left(\frac{1}{IP_{slab}} + \frac{1}{IP_{at}}\right)x^3}$$

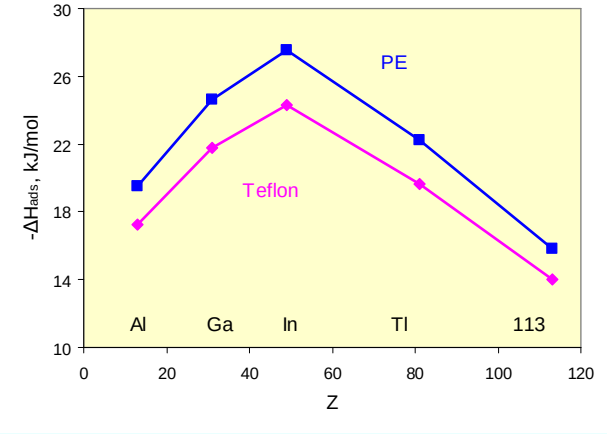


Calculations of atomic properties - IP, α and $x \sim R_{vdW}$

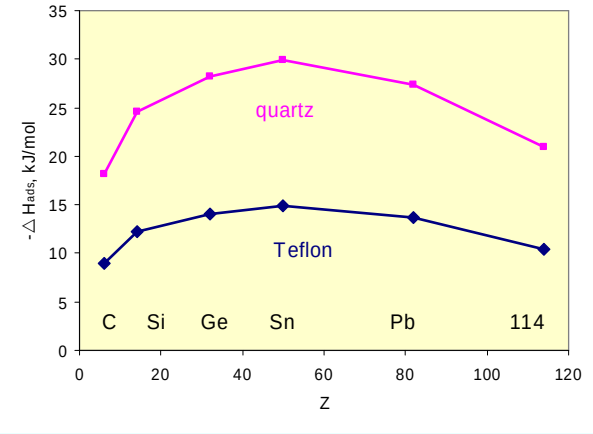
Method	Hg			112			
	AR, a.u.	α, a.u.	IP, eV	AR, a.u.	α, a.u.	IP, eV	Ref.
4*c*-DFT(B88/P86)	3.430	-	-	3.260	-	-	Anton
DC(B) CCSD(T)	-	34.15	10.445	-	27.64	11.97	Borschev./Eliav
exp.	3.429	33.92	10.4375	-	-	-	

Adsorption on Inert Surfaces of Group 13 ...18 Elements

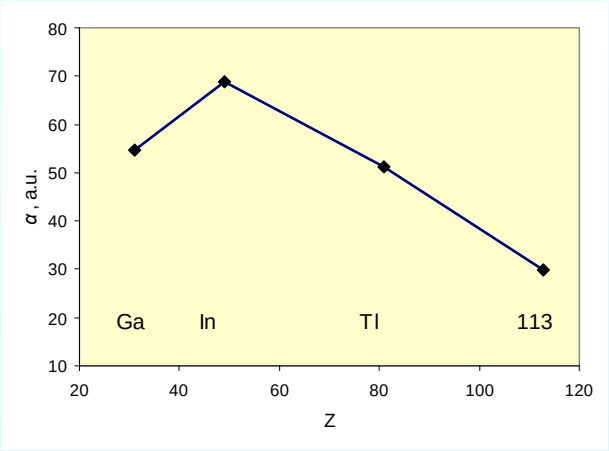
Group 13



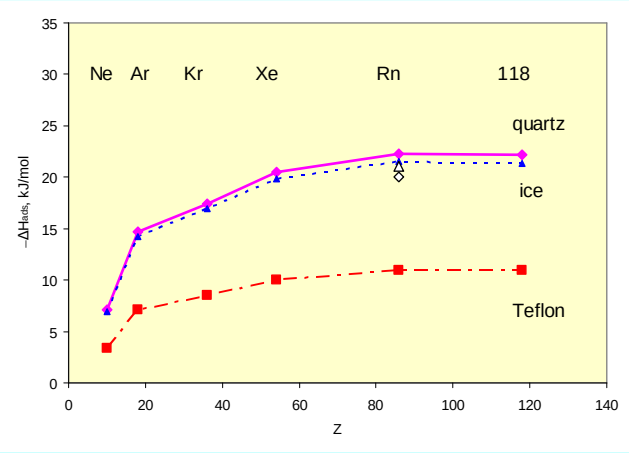
Group 14



Polarizability



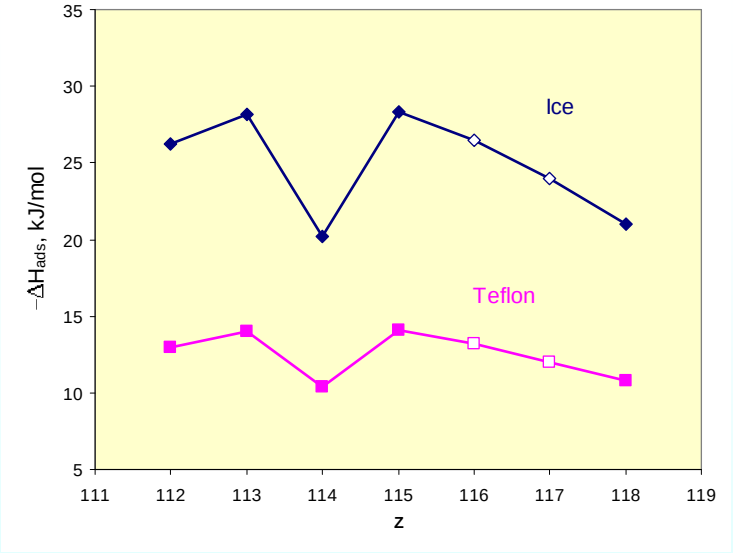
Group 18

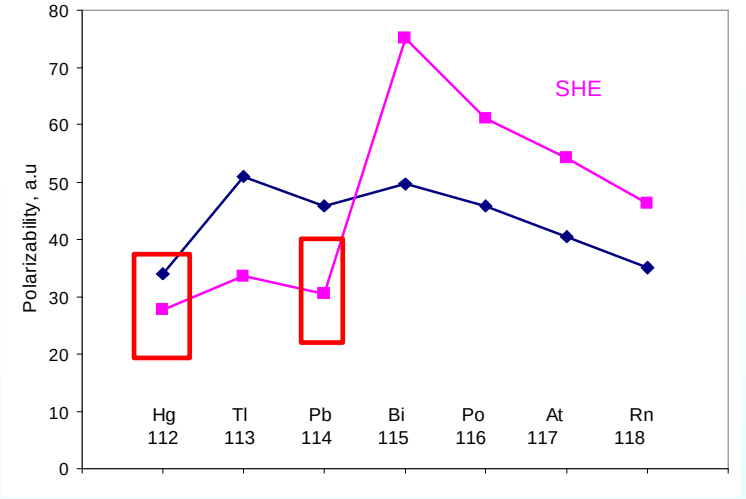


Atomic Properties of Elements 112, 113 and 114 and Adsorption on Inert Surfaces

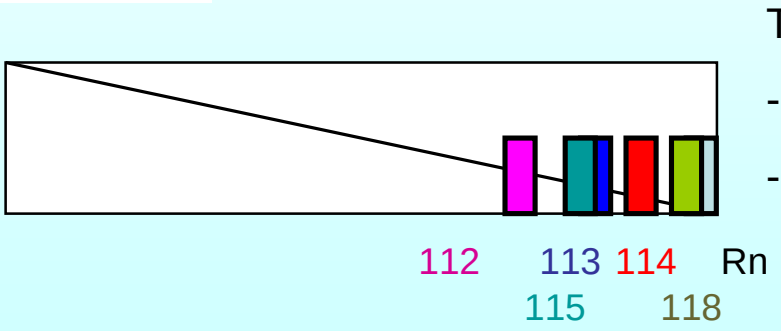
Property	112	113	114	115	...	118	Rn
Electr. conf.	$d^{10}s^2$	$s^2p_{1/2}^1$	$s^2p_{1/2}^2$	$s^2p_{1/2}^2\ p_{3/2}^1$	...	$s^2p_{1/2}^2\ p_{3/2}^4$	s^2p^6
IP, eV	11.97	7.31	8.54	5.58		8.91	10.75
α, a.u.	27.4	29.9	29.5	82.0		46.3	35.8
AR, a.u.	3.21	1.22	3.30	4.26		4.55	4.29
R_{vdW}, a.u.	3.75	1.84	3.94	5.09		4.55	4.29
ΔH_{ads}(i), kJ/mol	26.2	~28.2	20.2	~28.3		21.0	~20
ΔH_{ads}(T), kJ/mol	13.2	14.0	10.4	14.1		10.8	10.7

Adsorption of SHE on Inert Surfaces





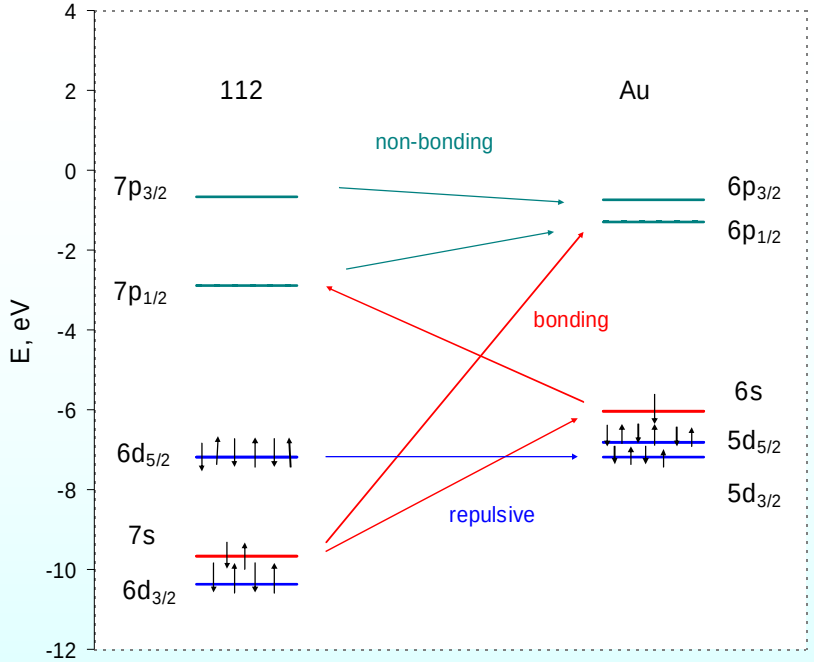
Adsorption on ice:

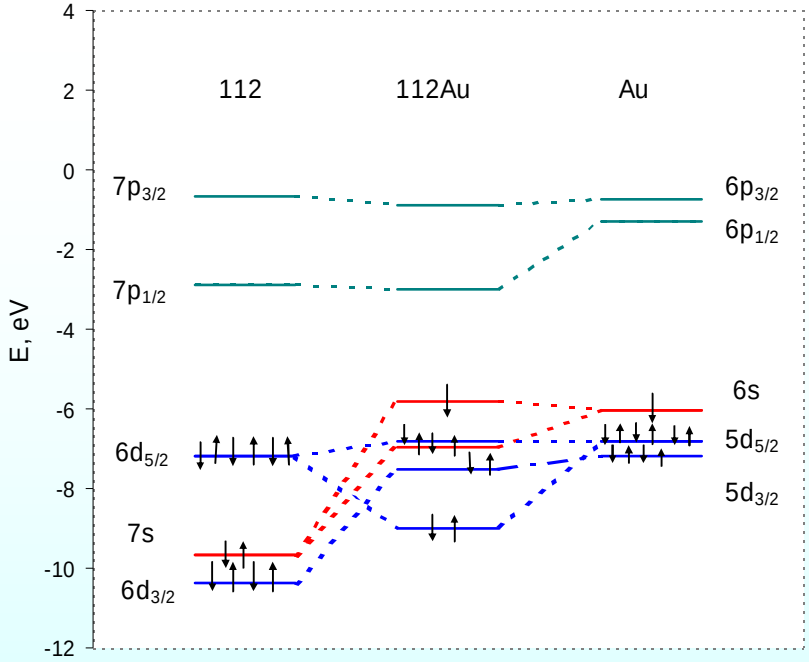


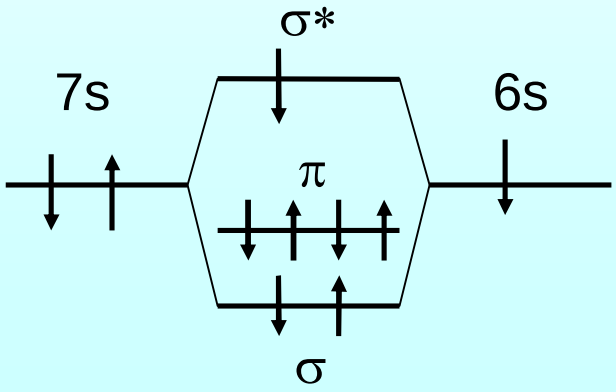
Adsorption of Elements 112, 113 and 114 on Gold

- Calculations of the interaction energy with Au
  - MAu
  - MAu_n for Au(100) and Au(111)

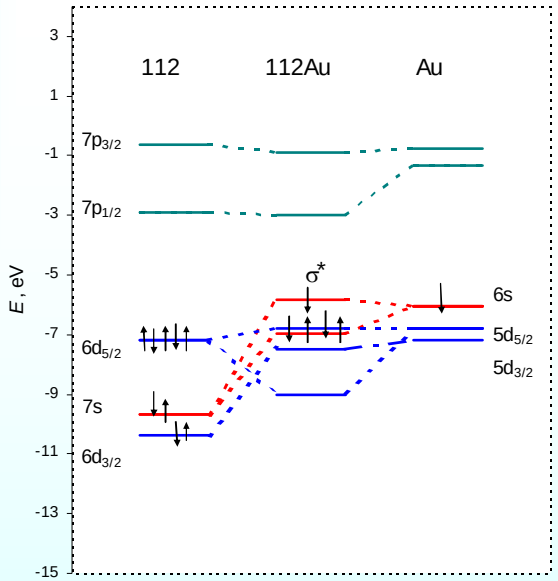
Chemical Bond Formation in 112Au

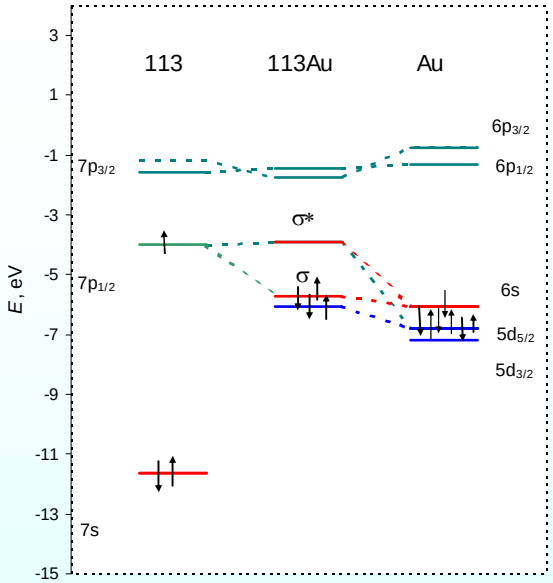


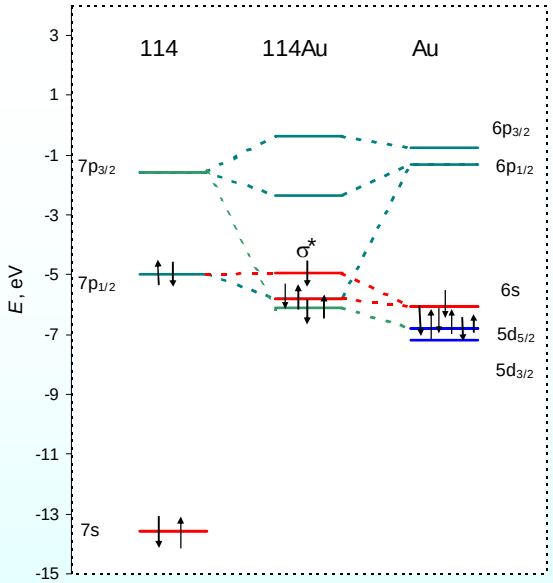


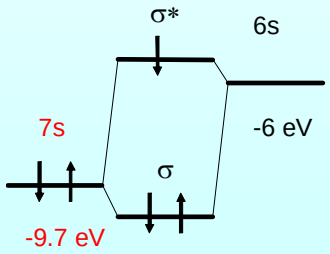


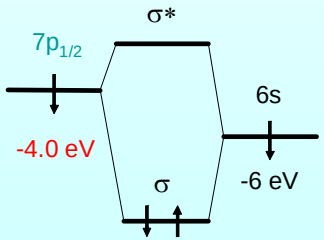
MO Formation in MAu (M = 112, 113 and 114)

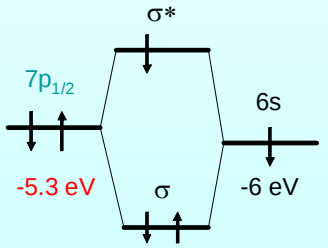








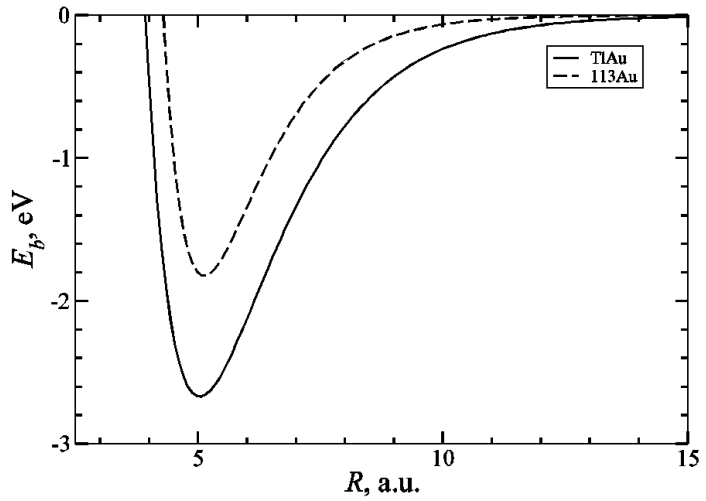




D_e 0.51 1.83 0.73 eV

Interaction of Element 113 with Gold

Molecule	D_e, eV	R_e, Å	w_e, cm^{-1}
TlAu	2.67	2.668	141
113Au	1.83	2.716	144

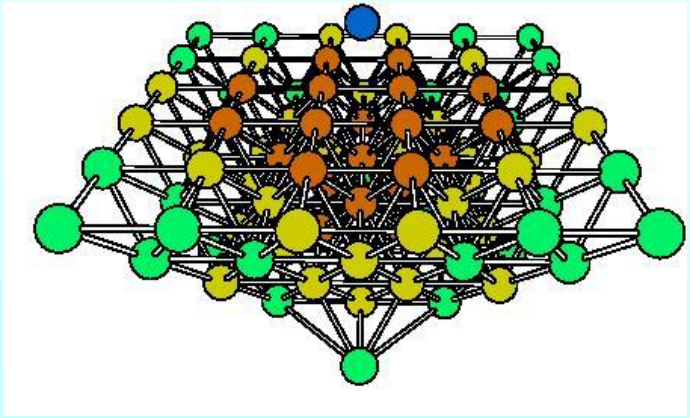


Potential energy curves for TlAu and 113Au

Cluster Calculations M-Au_n

- Au(100)
  - MAu_n and $MAu_nAu_{m(}$ n= 36; m = 156) – too binding
    - C. Sarpe-Tudoran *et al*. J. Chem. Phys. 126, 174702 (2007)

- Au(111)
  - MAu_n (from n=1 to n=120, convergence) - better
    - V. Pershina *et al*. J. Chem. Phys. 131, 084713 (2009)



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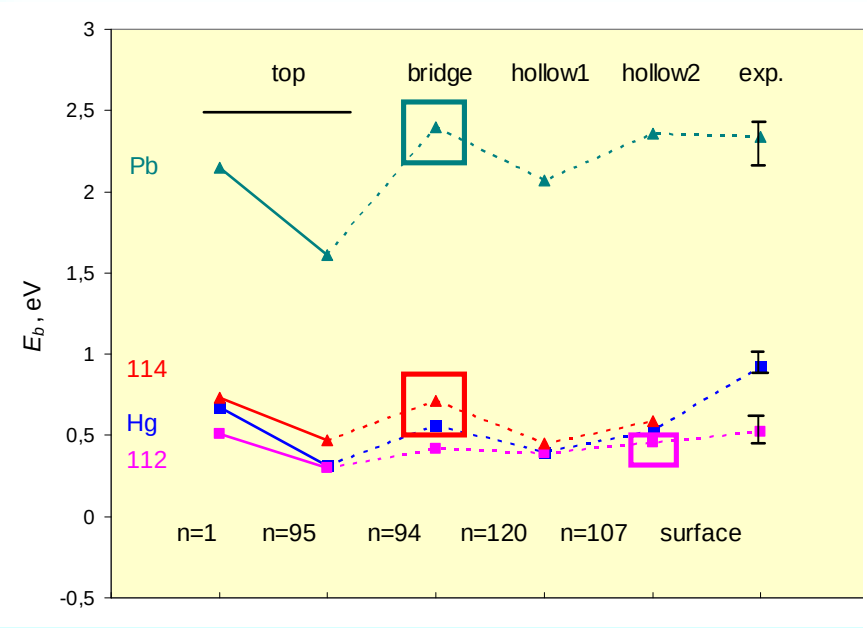
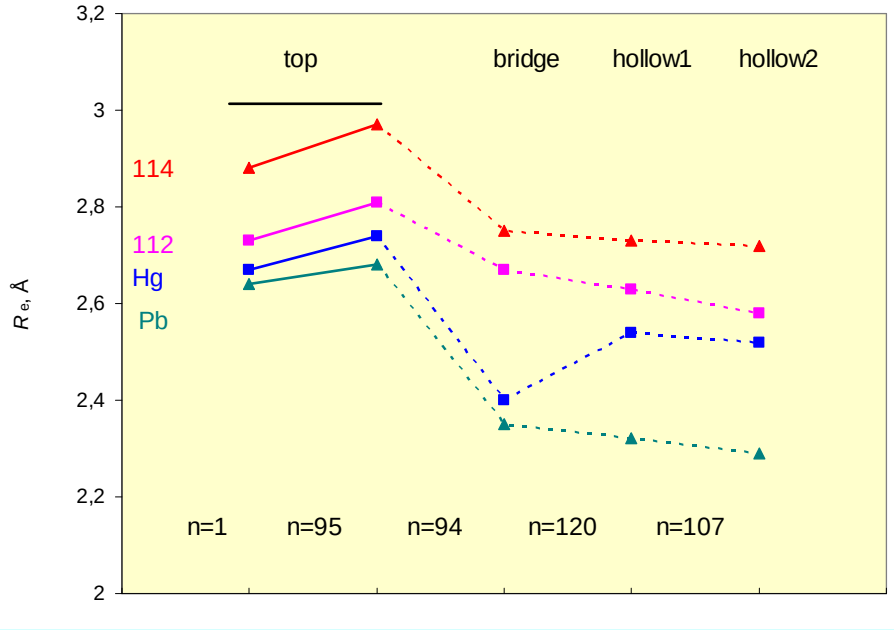
Binding Energies and Bond Lengths in M-Au_n for Au(111)





E_b: Pb >> 114 > Hg > 112

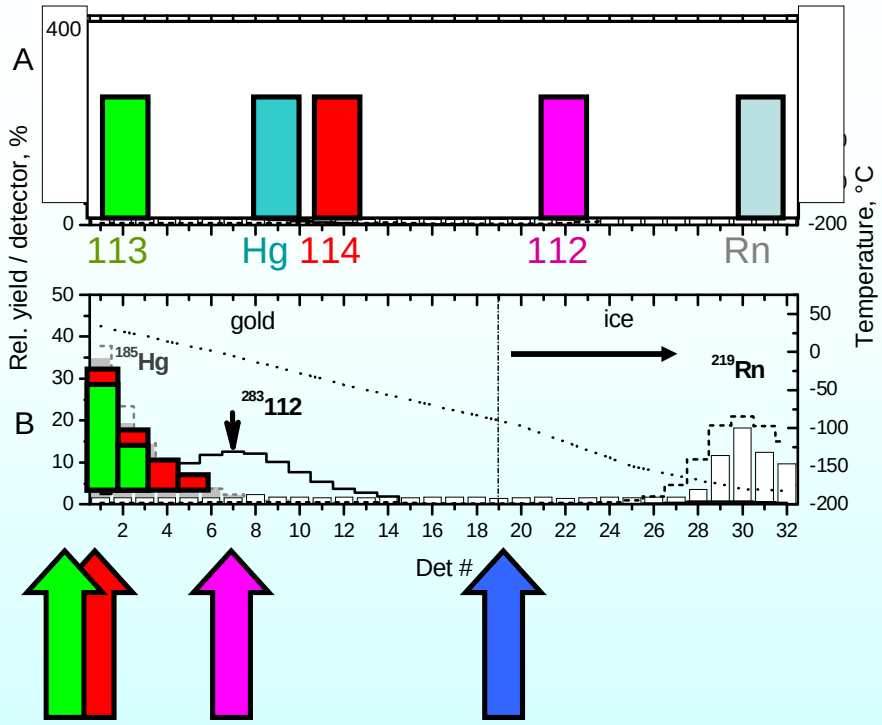
Predictions of ΔH_{ads} of Hg, E112, Pb and E114 on gold

	E_b(M-Au$_n$)				-ΔH_{ads}			
M	top	bridge	hollow1	hollow2	predictions		experiment	
	n=95	n=94	n=120	n=107	value	Ref.	value	Ref.
Hg	0.31	**0.56**	0.40	0.53	**0.56**[a]	this	**0.92**	B. Eichler
					1.01	Rossbach	1.02 ± 0.03	Soverna
112	0.30	0.42	0.39	**0.46**	**0.46**	this	**0.54** ± 0.04	R. Eichler
					0.12	Rossbach		
Pb	1.61	**2.40**	2.07	2.36	**2.40**	this	**2.43**	Haennsler
					2.27	Rossbach	2.37	B. Eichler
114	0.47	**0.71**	0.45	0.59	**0.71**	this	**0.36** $^{+0.2}$	R. Eichler
					0.95	Pershina		
					0.97	Rossbach		

[a] underestimated

E_b: Pb >> 114 > Hg > 112

Predictions of Gas-Phase Chromatography Behaviour of Elements 112, 113 and 114



113 114 112 114 exp. ?

112

Theory $-\Delta H_{ads} = 45$ kJ/mol

Exp. $-\Delta H_{ads}(\text{exp.}) = 52_{-3}^{+4}$ kJ/mol

R. Eichler, *et al*., 2007

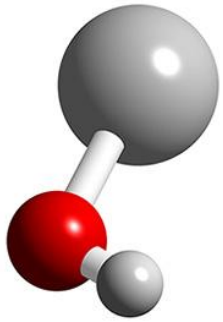
114

Theory $-\Delta H_{ads} = 70$ kJ/mol

Exp. $-\Delta H_{ads} = 35^{+19}_{-3}$ kJ/mol

R. Eichler, *et al*., 2008

TlOH and 113OH



M-OH

Bond lengths (R_e), dissociation energies (D_e) and vibrational frequencies (w_e)

Molecule	R_e, Å	D_e, eV	w_e, cm^{-1}
TlAu	2.69	2.67	141
113Au	2.72	1.83	144
TlOH	2.18	3.68	547
113OH	2.28	2.42	519

Adsorption enthalpies of M and MOH on gold

	$-\Delta H_{ads}$, kJ/mol			
Atom	M/Au	M-OH/Au	Exp. cond.	Ref.
Tl	240 ± 5	116 ± 2 114 ± 5 113 ± 4	He/H_2 O_2 on Au	König
113	159	?		our

Thank you for your attention !