Recent Achievements in the Electronic Structure Studies on the Heaviest Elements

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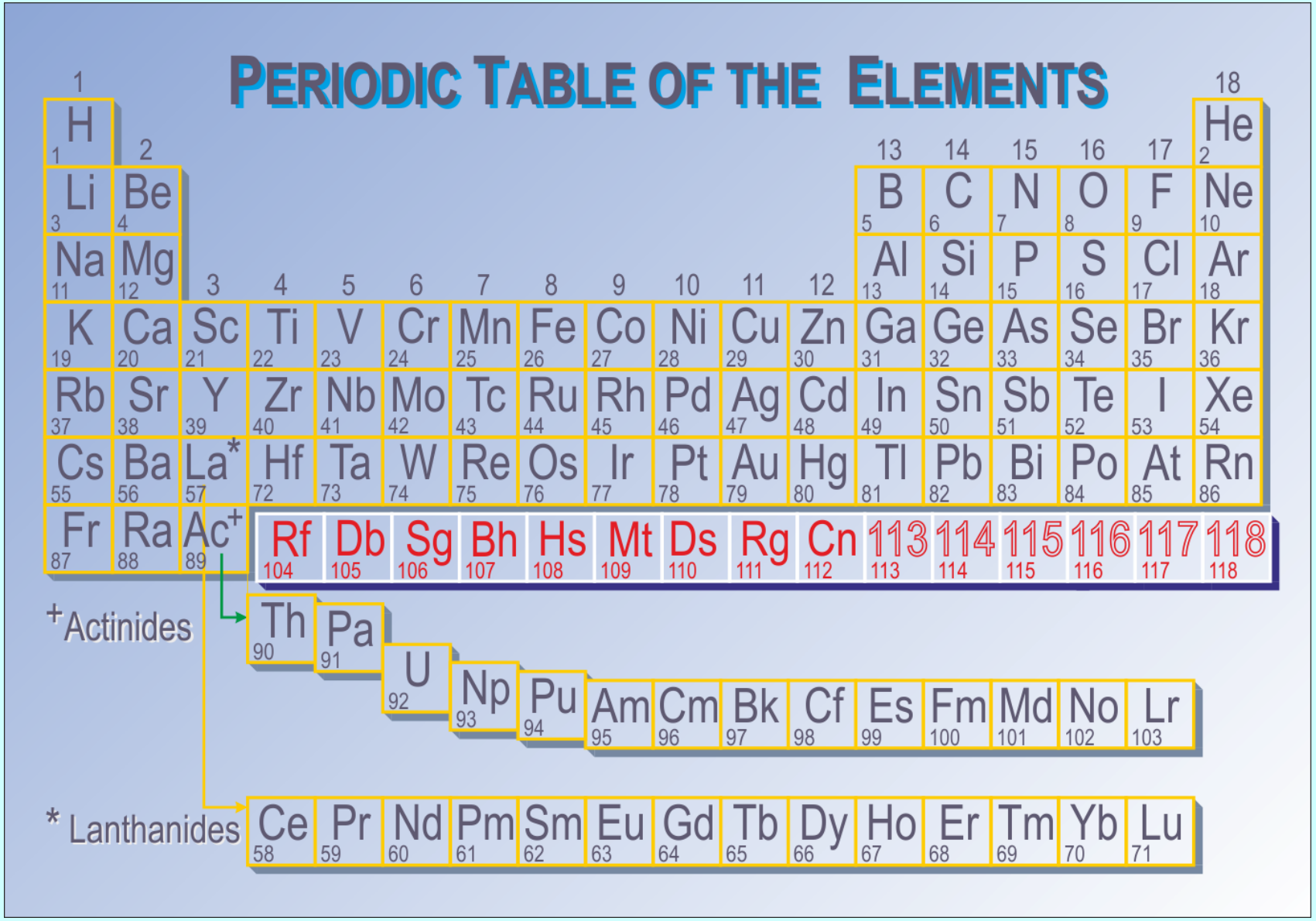
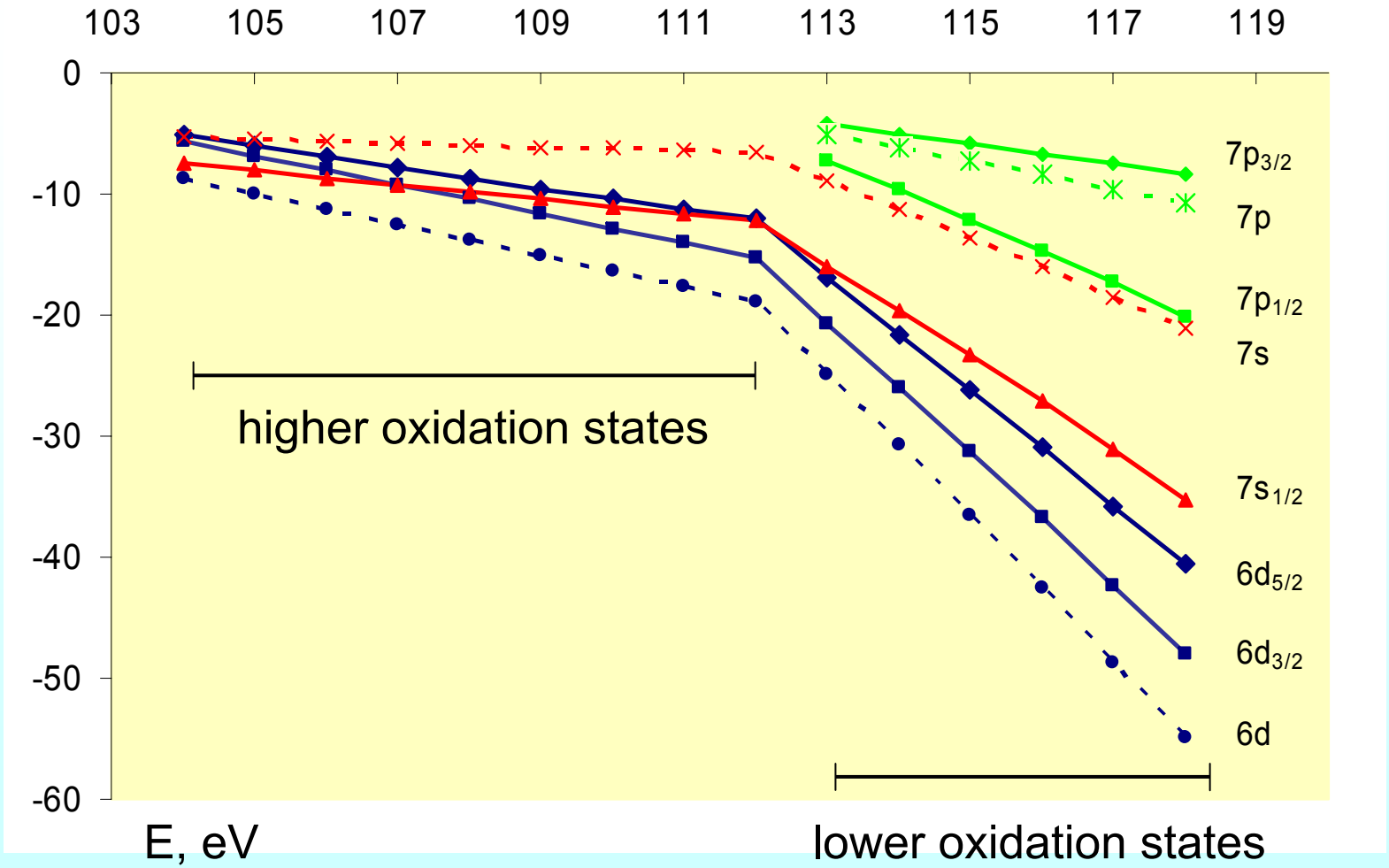

PERIODIC TABLE OF THE ELEMENTS
1 H 1
2 Li 3 Be 4
Na 11 Mg 12
3 4 5 6 7 8 9 10 11 12
13 B 5 C 6 14 N 7 15 O 8 16 F 9 17 18 He 2
Al 13 Si 14 P 15 S 16 Cl 17 Ar 18
K 19 Ca 20 Sc 21 Ti 22 V 23 Cr 24 Mn 25 Fe 26 Co 27 Ni 28 Cu 29 Zn 30 Ga 31 Ge 32 As 33 Se 34 Br 35 Kr 36
Rb 37 Sr 38 Y 39 Zr 40 Nb 41 Mo 42 Tc 43 Ru 44 Rh 45 Pd 46 Ag 47 Cd 48 In 49 Sn 50 Sb 51 Te 52 I 53 Xe 54
Cs 55 Ba 56 La* 57 Hf 72 Ta 73 W 74 Re 75 Os 76 Ir 77 Pt 78 Au 79 Hg 80 Tl 81 Pb 82 Bi 83 Po 84 At 85 Rn 86
Fr 87 Ra 88 Ac+ 89
Rf 104 Db 105 Sg 106 Bh 107 Hs 108 Mt 109 Ds 110 Rg 111 Cn 112 113 113 114 115 116 117 118
+Actinides
Th 90 Pa 91 U 92 Np 93 Pu 94 Am 95 Cm 96 Bk 97 Cf 98 Es 99 Fm 100 Md 101 No 102 Lr 103
* Lanthanides
Ce 58 Pr 59 Nd 60 Pm 61 Sm 62 Eu 63 Gd 64 Tb 65 Dy 66 Ho 67 Er 68 Tm 69 Yb 70 Lu 71

Relativistic DF and Nonrelativistic Energies of the Valence Orbitals (eV)



Modern Dirac Hamiltonian

- Dirac-Coulomb-Breit

$$\phi_{nkm} = \begin{bmatrix} \varphi \\ \overline{\varphi} \end{bmatrix} = \begin{Bmatrix} \frac{P_{nk}(r)}{r} \Upsilon_{km}(\vec{r},\xi) \\ i\frac{Q_{nk}(r)}{r} \Upsilon_{-km}(\vec{r},\xi) \end{Bmatrix}$$

- Electron correlation
  - Configuration Interaction (CI)
  - MBPT (MP2)
  - Coupled Cluster Single Doubles (CCSD (T))

$$h_D(i) = c\vec{\alpha}\vec{p} + \beta mc^2 + V_{nuc}$$

$$H_{DCB} = \sum_i h_D(i) + \sum_{i<j} (1/r_{ij} + B_{ij})$$

$$B_{ij} = -\frac{1}{2}\left[\vec{\alpha}_i\vec{\alpha}_j + (\vec{\alpha}_i\vec{r}_{ij})(\vec{\alpha}_2\vec{r}_{ij})/r_{ij}^2\right]/r_{ij}$$

$$\vec{\alpha}\vec{p} = -i\hbar\left(\alpha_1\frac{\partial}{\partial x_1} + \alpha_2\frac{\partial}{\partial x_2} + \alpha_3\frac{\partial}{\partial x_3}\right)$$

- QED effects
  - perturbatively

Relativistic Methods used for SHE Atoms

- DC(B) (meV)
  - FSCC, CCSD(T) (Eliav, Kaldor, Borschevsky)
  - QED - PT (Goidenko, Eliav...)
    - corrections (Herr.,Schwerdt.)
- MCDF (~0.1 eV)
  - Fricke, Johnson
  - Pyper, Grant
  - Nefedov
  - Indelicato, Pyykkö (Breit -SCF, QED-PT)
- DF (Fricke)
- DFT+QED

Systems

- IP: 103, 104, 111-122
  EA, α: 113-122
- EA(118)
  - 1% IP: 111-113, 118-120

- IP(0-Z^+): 103-108, 112,114
- IP(0): 113-119
- El. conf. (M): 119-164
- El. conf. (M^{Z+}): 119-121 ... 168

- IP: 104-172
- El. conf.: 121-131

Relativistic Methods used for SHE Molecules

- *ab initio* DF/DC (CI, MP2,CCSD)
  (DIRAC10) (Faegri, Saue, Borsch.)
- ECP
  - RECP+CCSD(T) (Lee, Nash)
  - PP + CCSD(T) (Schwerdtfeger)
- RDFT
  - 4c-DFT (Anton)
  - 4c-BDF (Liu)
  - 2c-DFT (van Wüllen)
  - SO ZORA (ADF)
- Solid state DFT (Schwerd.-group)

- Small systems
  - RgH, CnAu
- Larger mol-s
  - SgO_2Cl_2, $114F_4$
- Mol-s, compl., clusters
  - SgO_2Cl_2, $CnAu_n$, $SgO_n(H_2O)_mL_y^{q-}$, etc.
- Solid 112, 114

Predicted Ground States for SHEs

Method	121	122	123	124 ...	140	Ref.
DCB FSCC	8p	7d8p	-	-	-	Eliav
MCDF (OL)	-	-	-	-	$5g^{15}8p^{4}6f$	Indelicato
MCDF (AL)	8p	7d8p	$6f^{2}8p$	$6f^{2}8p^{2}$	$5g^{14}6f^{3}7d8p^{2}$	Nefedov
MCDF (AL)	8p	$8s^{2}$ (2+)	$6f^{1}$ (4+)	$6f^{1}$ (5+)	$5g^{16}8p^{2}$ (2+)	Pyykkö
DF	8p	7d8p	6f7d8p	$6f^{3}8p$	$5g^{14}6f^{3}7d8p^{2}$	Fricke
DF	8p	7d8p	6f7d8p	$6f^{2}7d8p$	$5g^{18}7d^{3}$	Nefedov
DFT + QED	8p	$8p^{2}$	6f7d8p	$6f^{2}8p^{2}$	-	Umemoto

No highly accurate FSCC calculations for Z > 122

MCDF(OL) are restricted due to computer limitations

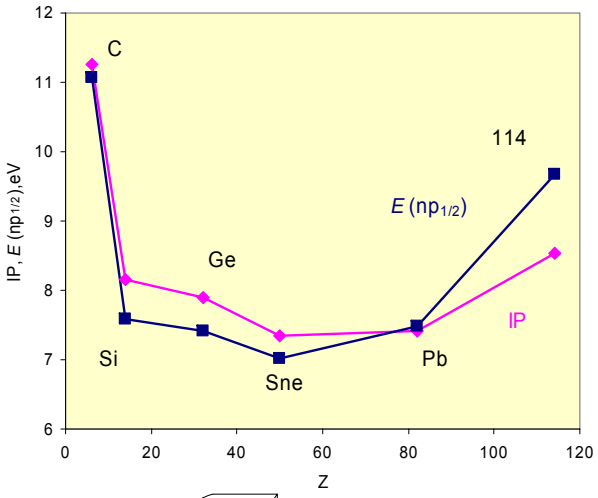
MCDF + Breit + QED: confirmed the end of the PT with Z = 173 [$E(1s) < -2mc^2$]

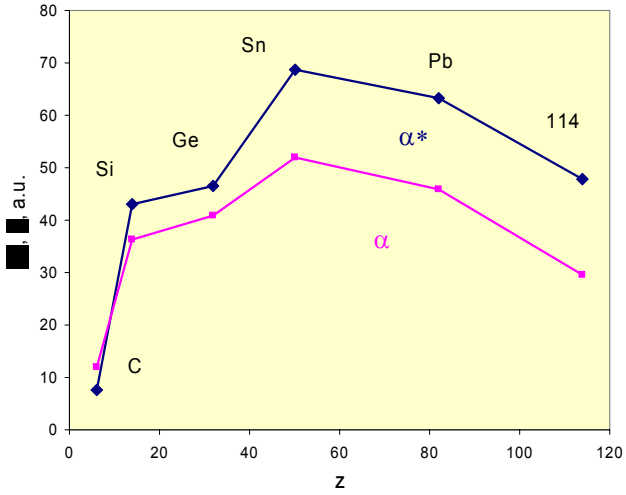
[P. Indelicato, Theor. Chem. Acc. 129, 495,(2011)]

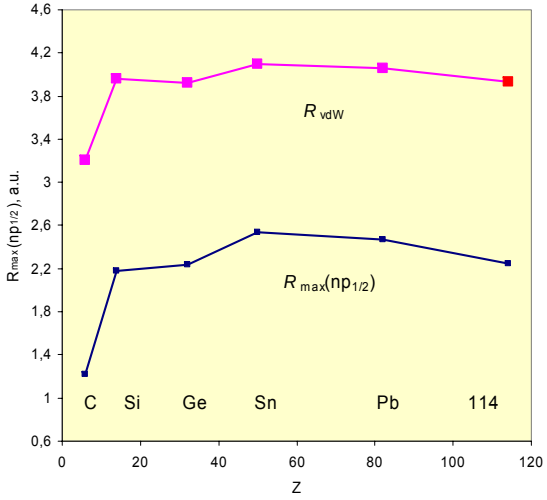
Predictions for Experiments

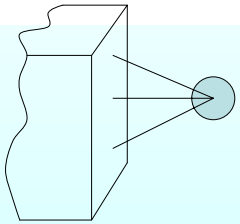
- Transport through cappilaries: ΔH_{ads}
- Stability of compounds and ΔH_f
- Adsorption: ΔH_{ads}, T_{ads}
- Complex formation constants K_i
- Distribution coefficients K_d
- Redox potentials

Atomic Properties of Group 14 Elements and Adsorption on Inert Surfaces



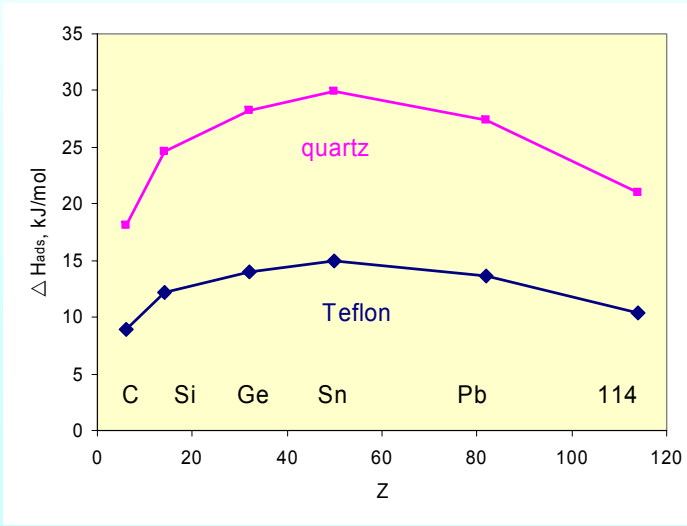






$$E(x) = -\frac{3}{16}\left(\frac{\varepsilon - 1}{\varepsilon + 2}\right)\frac{\alpha_{mol}}{\left(\frac{1}{IP_{slab}} + \frac{1}{IP_{at}}\right)x^3}$$

ΔH_{ads}, kJ/mol	C	Si	Ge	Sn	Pb	114	112
Ice	17.56	23.65	27.13	28.76	26.29	20.20	26.2
Teflon	8.91	12.22	14.04	14.94	13.65	10.41	16.4
					13(exp.)		



Predictions of Adsorption on Inert Surfaces

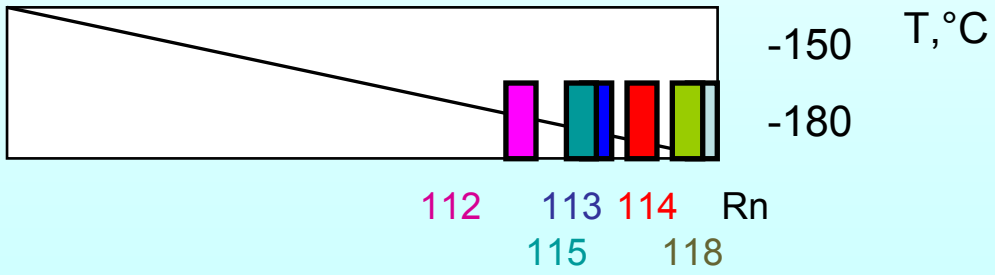
An atom-slab model:

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

DC(B) calculations of IP, α, etc.

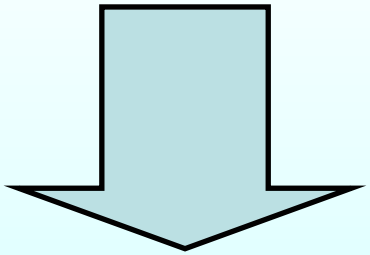
Property	112	113	114	115	...	118	Rn
Electr. conf.	$d^{10}s^2$	$s^2p_{1/2}^1$	$s^2p_{1/2}^2$	$s^2p_{1/2}^2\ p_{3/2}^1$	...	$s^2p_{1/2}^2\ p_{3/2}^4$	s^2p^6
ΔH_{ads}(i), kJ/mol	26.2	~28.2	20.2	~28.3		21.0	~20
ΔH_{ads}(T), kJ/mol	16.4	14.0	10.4	14.1		10.8	10.7

Adsorption on ice



Bonding (Chemical) of SHEs

- Molecules
- Interaction with surfaces
- Solid state

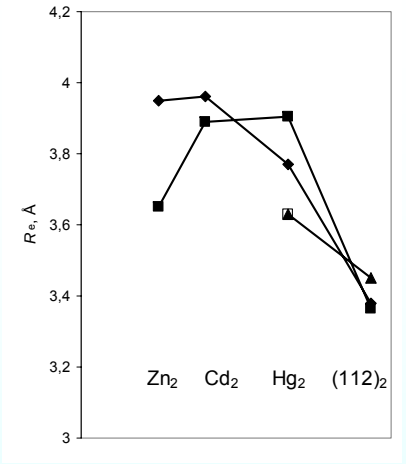


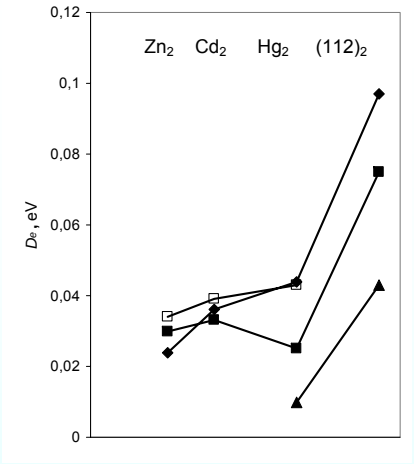
predictions and interpretation of experiments

Accuracy of Different Methods for 111H

Molecule	Method	R_e	Ref.
AuH	Experiment	1.5236	Seto
RgH	DC CCSD(T)	1.522	Thierf., Schwerdt.
	SO PP CCSD(T)	1.499	Seth, Schwerdt.
	PP CCSD(T)	1.529	Dolg, Schwerd.
	SC-PP CCSD(T)	1.506	Han, Hirao
	ADF ZORA	1.543	Pyykkö
	DC PBE	1.558	Thierf., Schwerdt.
	4*c*-BDF	1.546	Liu, van Wüllen
	4*c*-DFT	1.520	Anton

Comparison of Various Calculations for Group 12 M_2





QR PP CCSD(T)

4*c*-BDF PBESIC

4*c*-DFT(P88/B86)

Spectroscopic properties: bond lengths, R_e, (in Å) and dissociation energies, D_e, (in eV) of Hg_2 and $(112)_2$

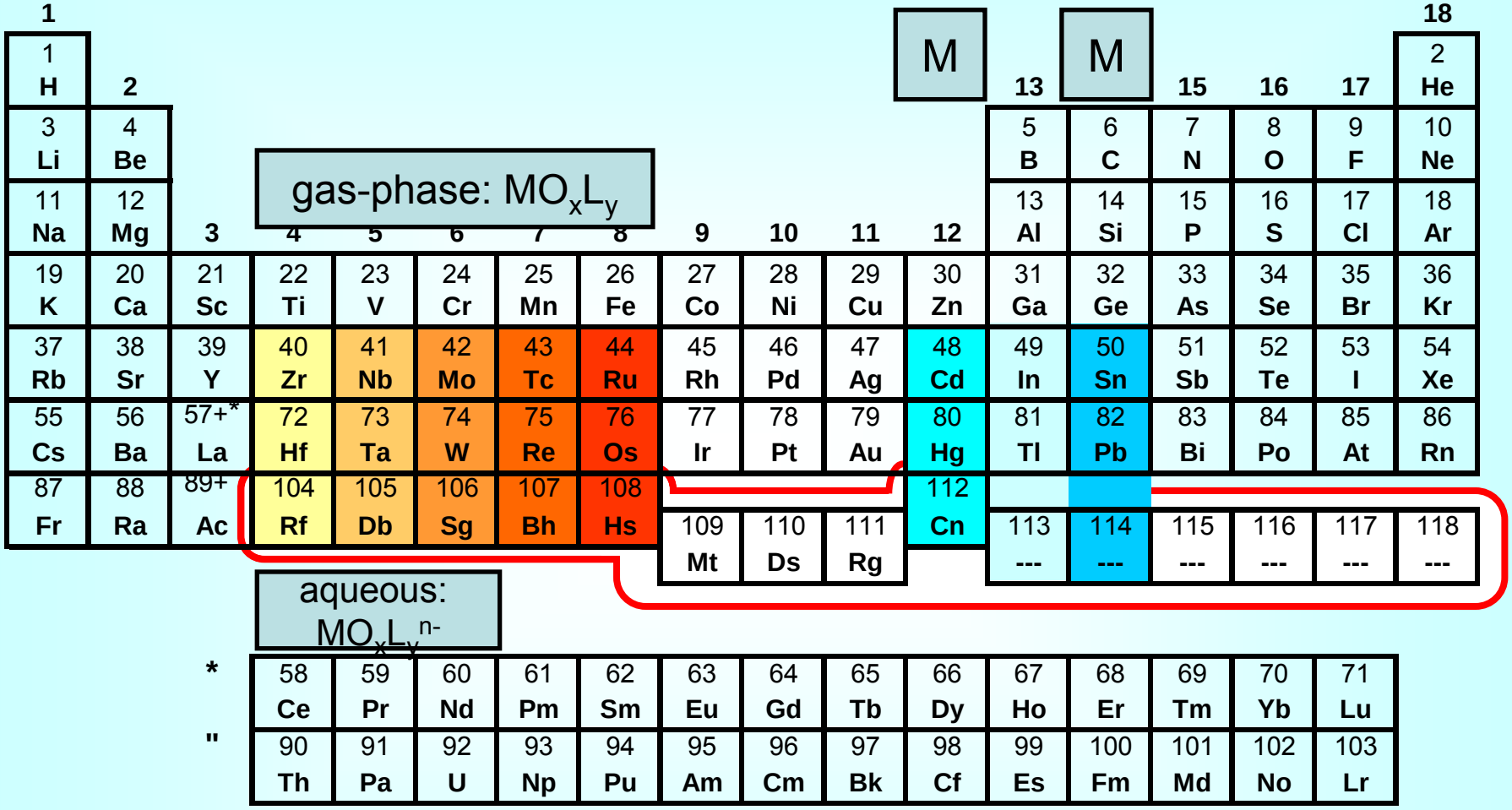
Method	Hg_2		$(112)_2$		Reference
	R_e	D_e	R_e	D_e	
4*c*-BDF PBE	3.439	0.053	3.089	0.156	Liu
4*c*-BDF PBESIC	3.904	0.025	3.363	0.075	Liu
4*c*-DFT(B88/P86)	3.63	0.01	3.45	0.05	Anton
QR-PP CCSD(T)	3.769	0.044	3.386	0.097	Dolg, Schwerdtfeger
Experiment	3.63	0.043	-	-	Zee, Huber and Herzog

Comparison of Different Calculations for HgAu and CnAu

Method	HgAu			CnAu			Ref.
	R_e, Å	D_e, eV	w_e, cm^{-1}	R_e, Å	D_e, eV	w_e, cm^{-1}	
DF (X2C) FSCC	2.634	0.46	120	2.704	0.41	95	Borschevskii (this) (DIRAC08)
ARECP+ UCCSD(T)+SO	2.653	0.53	116	2.727	0.39	95	Zaitsevskii [1] (Gaussian03)
DFT-SO (B98)	2.713	0.51	104	2.774	0.36	83	Zaitsevskii[1] (NWCHEM code)
4c-DFT (B88/P86)	2.67	0.67	99	2.73	0.51	74	Pershina[4]
2c-DFT (BP)	2.68	0.62	-	2.73	0.47	-	van Wüllen[5]
2c-DFT (PBE0)	2.68	0.56	-	2.74	0.39	-	van Wüllen[5]

1. A. Zaitsevskii, *et al*. Centr. Eur. J. Phys. **4**, 448 (2006)
2. R. Wesendrup and P. Schwerdtfeger, Angew. Chem. Int. Ed. **39**, 909 (2000)
3. Z. J. Wu, Chem. Phys. Lett. **406**, 24 (2005)
4. V. Pershina, *et al*. J. Chem. Phys., 2010, in print
5. A. Zaitsevskii, *et al*. J. Chem. Phys. **132**, 081102 (2010)

Chemically Studied Systems of SHEs



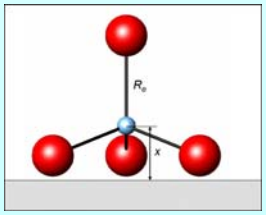
Summary of Gas-Phase Adsorption Studies for d-Elements

Group	Compounds	Theoretically predicted volatility	Experimentally observed volatility	Problem solved
4	MCl_4, MBr_4	Hf < Rf	Zr > Hf < Rf	?
5	MCl_5	Nb < Ta < Db	Ta > Db ($DbOCl_3$)	
	MBr_5	Nb < Ta < Db	Nb > Ta > Db	
6	MO_2Cl_2	Mo > W > Sg	Mo > W > Sg	Yes
7	MO_3Cl	Tc > Re > Bh	Tc > Re > Bh	Yes
8	MO_4	Ru < Os > Hs	Os > Hs	Yes

Group 6, 7 and 8 Oxyhalides

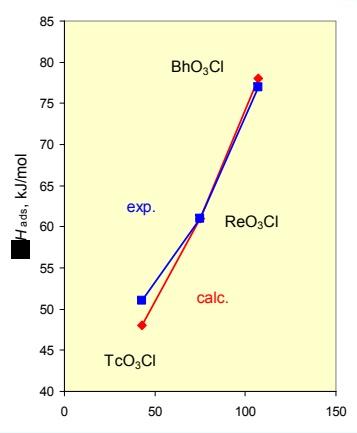
- Group 6
  - MO_2Cl_2
- Group 7
  - MO_3Cl

- Group 8
  - MO_4



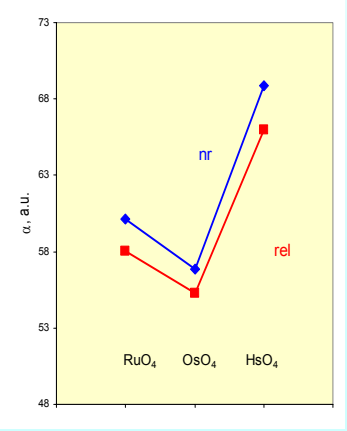
$$E(x) = -\frac{2Qe\mu_{mol}^{\ 2}}{x^2} - \frac{Q^2e^2\alpha_{mol}}{2x^4} - \frac{3}{2}\frac{\alpha_{mol}\alpha_{Cl}}{\left(\frac{1}{IP_{mol}} + \frac{1}{IP_{Cl}}\right)x^6}$$

	TcO_3Cl	ReO_3Cl	BhO_3Cl
μ, D	0.93	1.29	1.95
$-\Delta H_{ads}$ (kJ/mol) calc.	48 ± 2	61 ± 2	78 ± 5
$-\Delta H_{ads}$ (kJ/mol) exp.	51 ± 2	61 ± 2	77 ± 8



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

Property	RuO_4	OsO_4	HsO_4	Ref.
α, a.u.	58.07	55.28	66.00	calc.
$-\Delta H_{ads}$ (kJ/mol) calc.	40.23	39.0	46.5	calc.
$-\Delta H_{ads}$ (kJ/mol) exp.	-	39 ± 1	46 ± 2	exp.



Possible Mechanisms of Adsorption of MBr_5 on Quartz

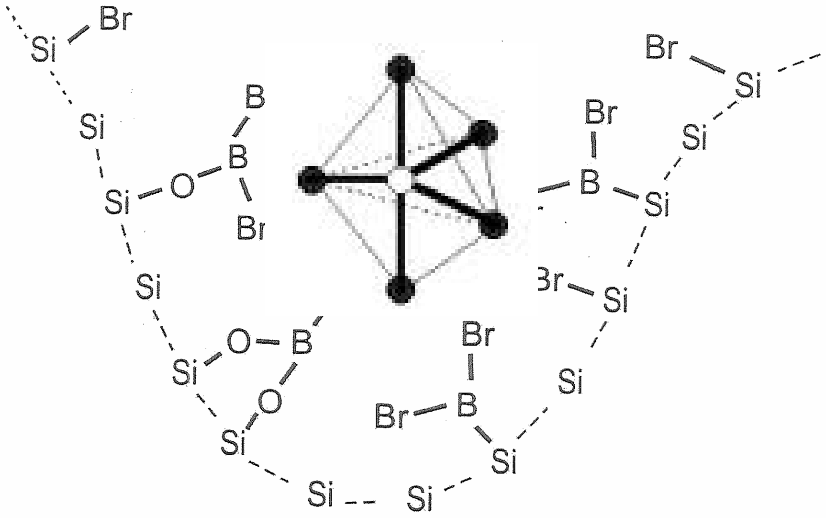
- Oxide/bromide formation:
  - in the gas-phase
    $M + O_2 + Br_2 = MOBr_3$
    $MOBr_3 + Br_2 = MBr_5$
  - on the surface
    $MBr_5 + 2Si_sOH = (Si_sO)_2MBr_3$
    (if the surface is not brominated)

- Adsorption
  - van der Waals on SiO_2-Br
  - salt formation: $MBr_5 + KBr$ (aerosol) = $KMBr_6$ (on the surface)

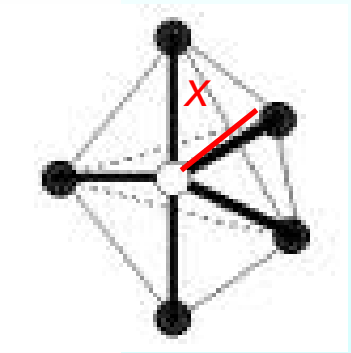
Adsorption of Bromides on Quartz Surface

van der Waals interaction:

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



Brominated SiO_2 surface



x - adsorption distance

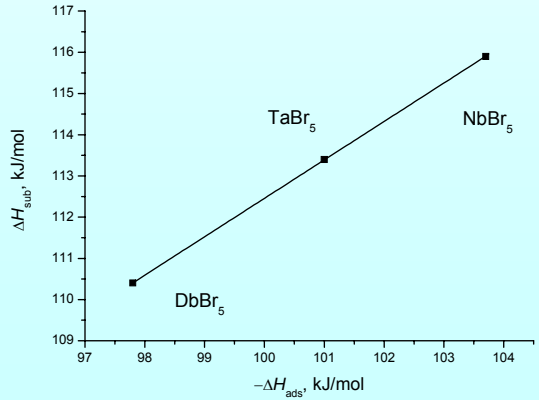
[I. Zvara, *The Inorganic Radiochemistry of Heavy Elements*, Springer, 2008]

Physisorption of MBr_5 on Brominated Quartz Surface

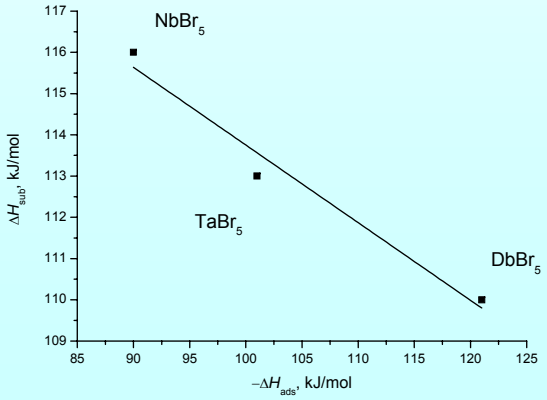
Property	$NbBr_5$	$TaBr_5$	$DbBr_5$	Trend in vol.
IP, eV	9.35	9.33	9.37	-
$<\alpha>$, a.u.	172.06	167.30	167.02	-
R_e(ax/eq), Å	2.500/2.449	2.495/2.444	2.548/2.496	-
x, Å	2.31	2.32	2.34	-
$-\Delta H_{ads}(SiO_2/Br)$, kJ/mol	103.7	101 ± 4	97.8	Nb < Ta < Db
$-\Delta H_{sub}(MBr_5)$, kJ/mol	115.9	113.4	(110.4)	Nb < Ta < Db
$-\Delta H_{ads}(SiO_2/KBr)$, kJ/mol [AT]	93 ± 4	101 ± 4	121 ± 11	Nb > Ta > Db
$-\Delta H_{ads}(SiO_2/KBr)$, kJ/mol [QZ]	89 ± 5	101 ± 5	71	Nb > Ta < Db

chemistry,

theory:



exp.:



Summary of Predictions

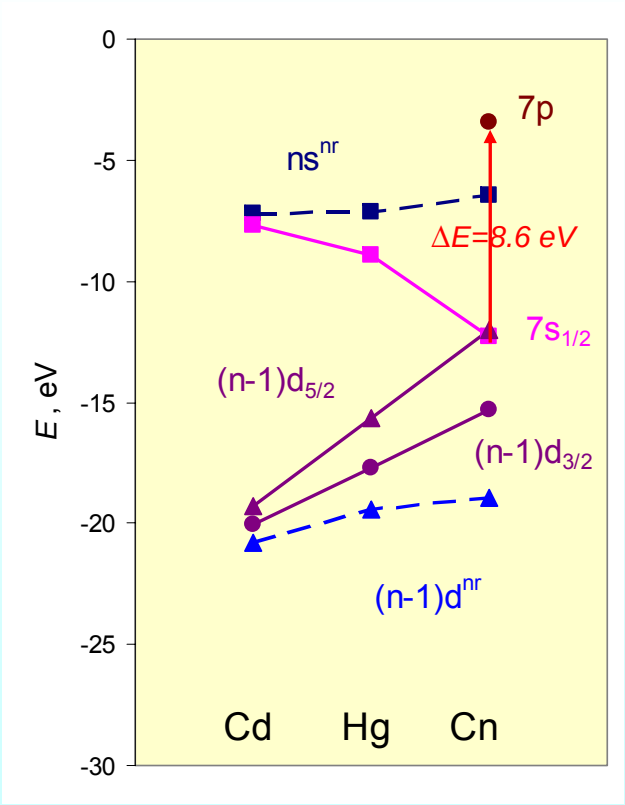
Mechanism	$-\Delta H_{ads}$
• MBr_5 formation	• Ta > Db > Nb
• vdW adsorption	• Nb > Ta > Db
• ΔH_{sub}	• Nb > Ta > Db
• Salt $KMBr_6$ formation	• Nb < Ta < Db
• [Surface oxide $(Si_sO)_2MBr_3$ formation]	• [Nb > Ta > Db]
• Early experiments	• Nb < Ta < Db
• Qin Zhi experiment	• Nb < Ta > Db

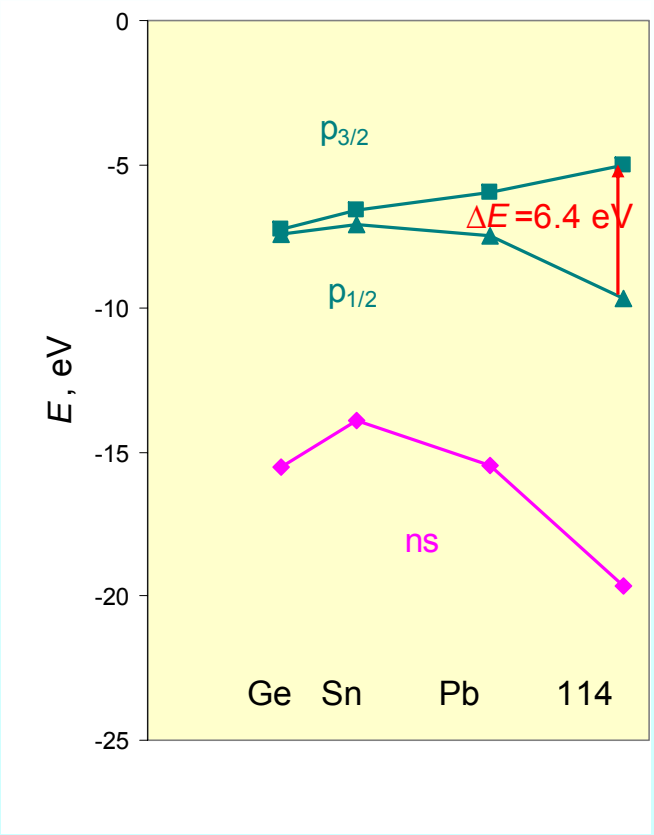
?

Volatility of E112-E114

[K. Pitzer, J. Chem. Phys. 1975]:

Cn ($6d^{10}7s^2$): $E(s^2 \rightarrow sp)$ = 8.6 eV $E114$ ($7s^27p_{1/2}^2$): $E(p_{1/2}^2 \rightarrow p^2)$ = 6.4 eV



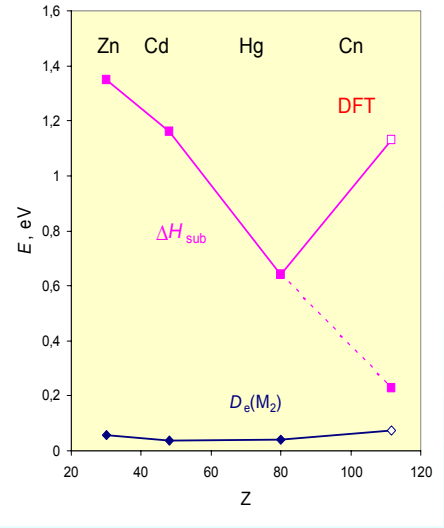


Predictions of ΔH_{sub} and ΔH_{ads} of M on Gold

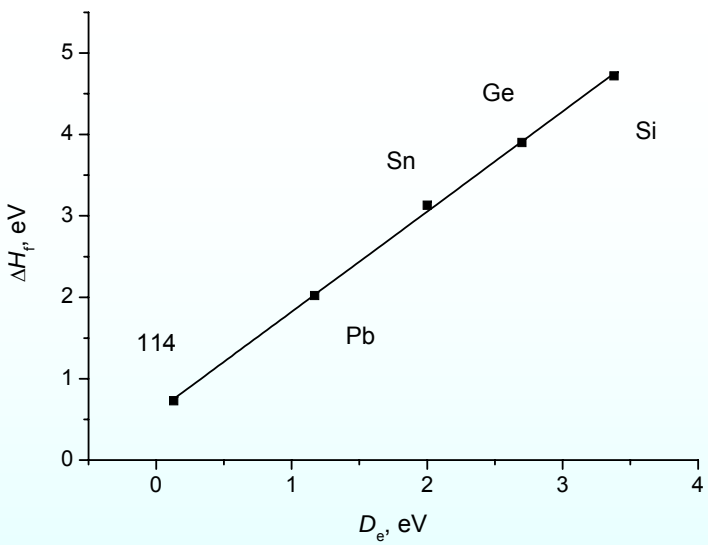
- ΔH_{sub}
  - extralpolation (not for group 12)
  - $\Delta H_{sub} = kD_e(M_2)$
  - solid-state cal-s: E_{coh}
- ΔH_{ads}
  - $\Delta H_{ads}(M) \approx kD_e(MAu)$
  - calculation of $E_b(M - Au_n)$
- ΔH_{sub} *vs.* ΔH_{ads}
  - $D_e(M_2)$ *vs.* $D_e(MAu)$

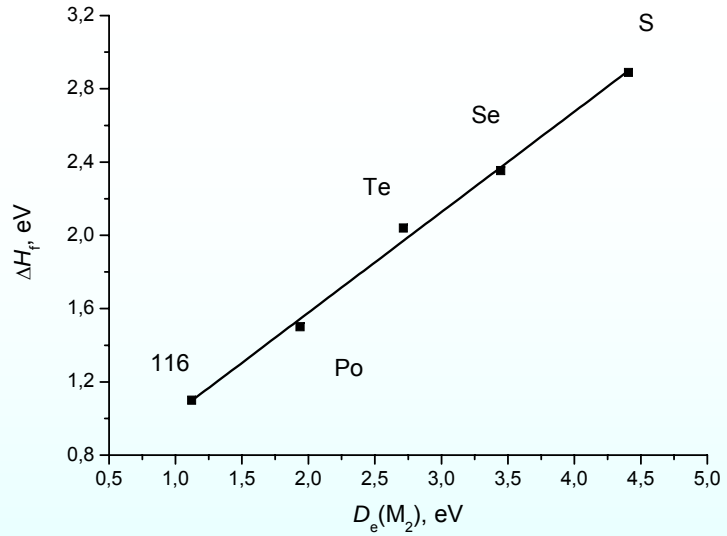
comparable results

comparable results



Predictions of $\Delta H_{sub} = kD_e(M_2)$





ΔH_{sub} (in kJ/mol)

Method	E112	E113	E114	E115	E116	E117	Ref.
Extrapolation	22.2	138.1	70.3	146.4	92.1	83.7	Keller, Eichler
Correlation	95	144.7	70.4	152 ± 12	101.3	91.7	Pershina
DFT cal-s	109	-	50	-	-	-	Gaston, Herr.

Solid State Calculations (DFT)

- E112
  - SR LDA: $E_{coh}(hcp)$ = 1.13 eV (Hg, *fcc*, 0.64 eV)

    (in agreement with $D_e(112)_2 > D_e(Hg_2)$)

    [N. Gaston, *et al*. Angew. Chem. Int Ed. 46, 1663 (2007)]

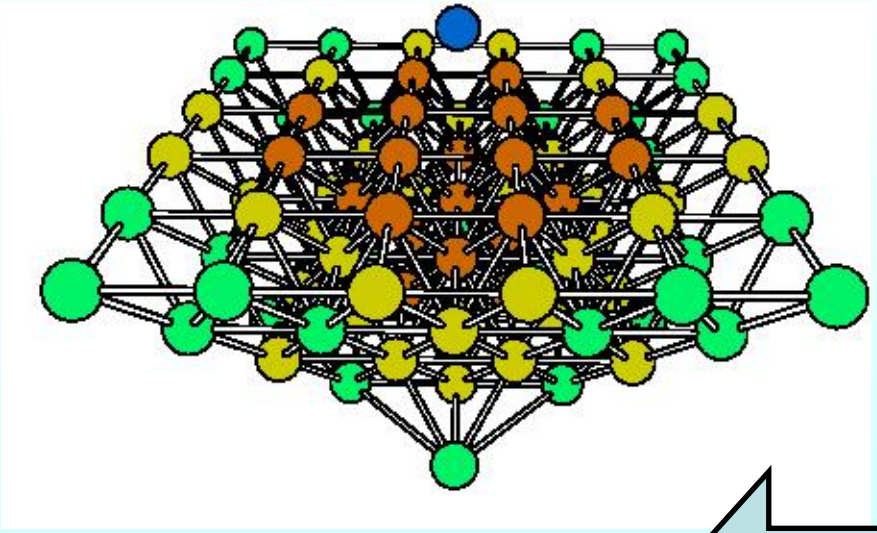
- E114
  - SR-PW91: $E_{coh}(fcc)$ = 3.021 eV
  - SO-PW91: $E_{coh}(hcp)$ = 0.504 (Pb, *fcc*, 2.02 eV)

    [A. Hermann, *et al*. Phys. Rev. B 82, 155116 (2010)]

$E_{coh}(112) > E_{coh}(114)$

Predictions of E_b(M-Au$_n$)

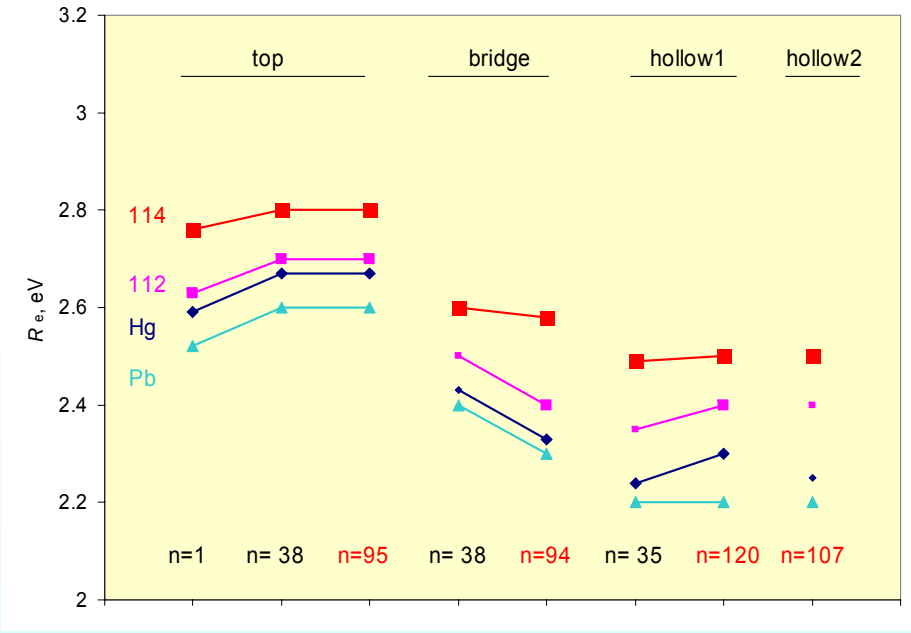
from n=1 to n = max (convergence in E_b)



4c-DFT calculations

J. Anton

Binding Energies and Bond Lengths in M-Au_n



ΔE_b(M-M') ≈ *const* for *n*= 1 till *n* = max

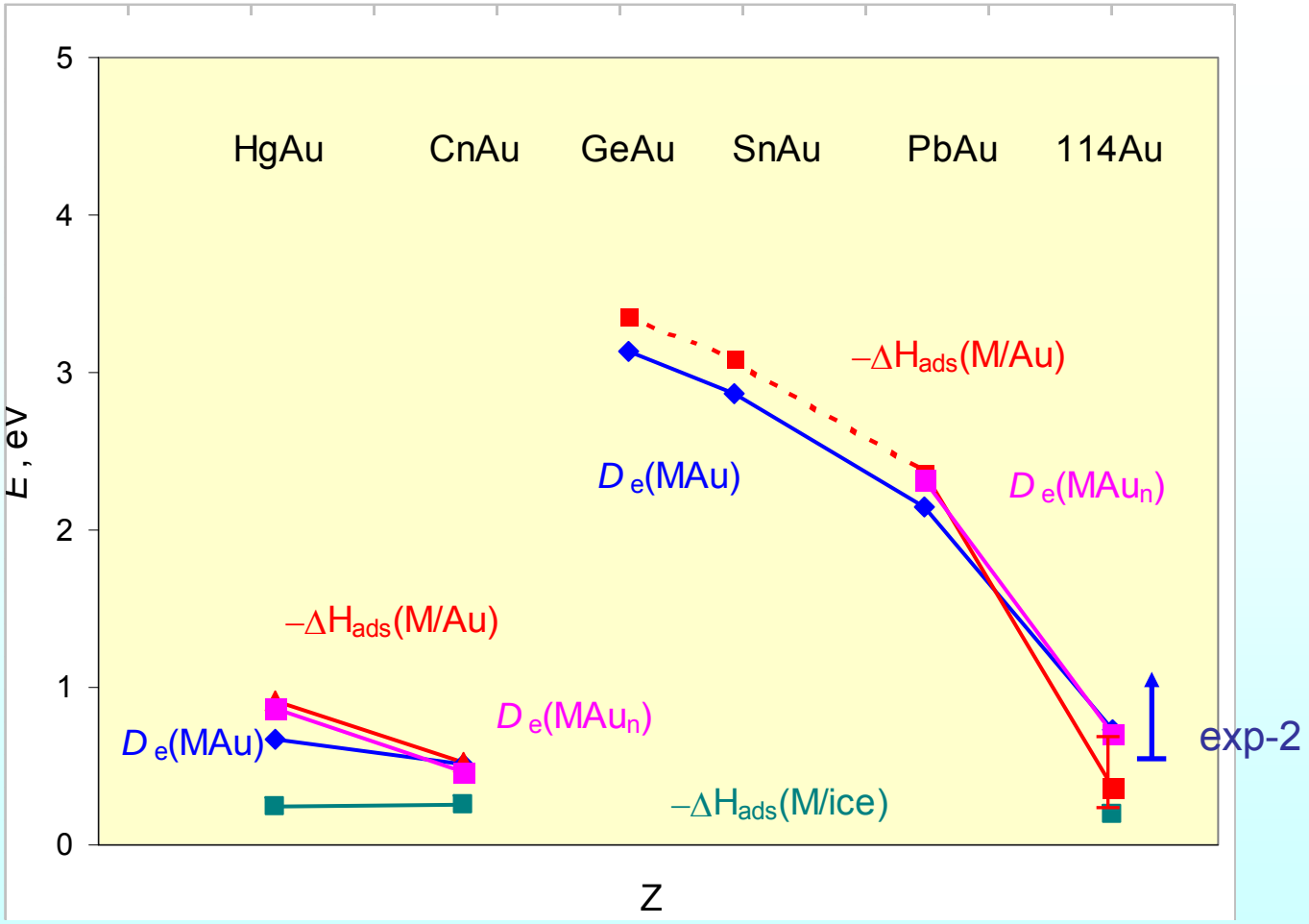
Comparison of Calculations for Cn-Au_n and 114-Au_n

Binding Energies (in eV) of Cn-Au_n and 114-Au_n for Au(100) and Au(111)

Method	n	Cn-Au_n	114-Au_n	Ref.
4c-DFT (B88/P86)	1	0.51	0.73	Pershina[1]
2c-DFT (B88/P86)	1	0.47	0.72	Rykova[2], Zaits.[3]
SO-DFT (B88/PW91)	3	0.47	0.77	Rykova[2], Zaits.[3]
RPP+2c-DFT (B88/P86)	26 (bridge) Au(100)	0.33	0.55	Zaitsevskii[4]
RPP+2c-DFT (B88/P86)	37 (hollow2) Au(111)	-	0.49	Zaitsevskii[3]
4c-DFT (B88/P86)	95 (hollow) Au(111)	0.30	0.47	Pershina[1]
-"-	94 (bridge) Au(111)	0.42	0.71	Pershina[1]
-"-	107 (hollow2) Au(111)	0.46	0.59	Pershina[1]
$-\Delta H_{ads}$(exp.)		0.54 ± 0.04	$0.36\ ^{+0.5}_{-0.1}$	Eichler[5]
			≥ Cn	Yakushev[6]

1. V. Pershina, *et al*. J. Chem. Phys. **131**, 084713 (2009).
2. E.A. Rykova, *et al*. J. Chem. Phys. **125**, 241102 (2006).
3. A. Zaitsevskii, C. van Wüllen, *et al*. Phys. Chem. Chem. Phys. **12**, 4152 (2010).
4. A. Zaitsevskii, *et al*. Russ. Chem. Rev. **78**, 1173 (2009).
5. R. Eichler, *et al*. Nature, **447**, 72 (2007).
6. A. Yakushev, to be published.

Comparison of M-Au Bonding in Groups 12 and 14

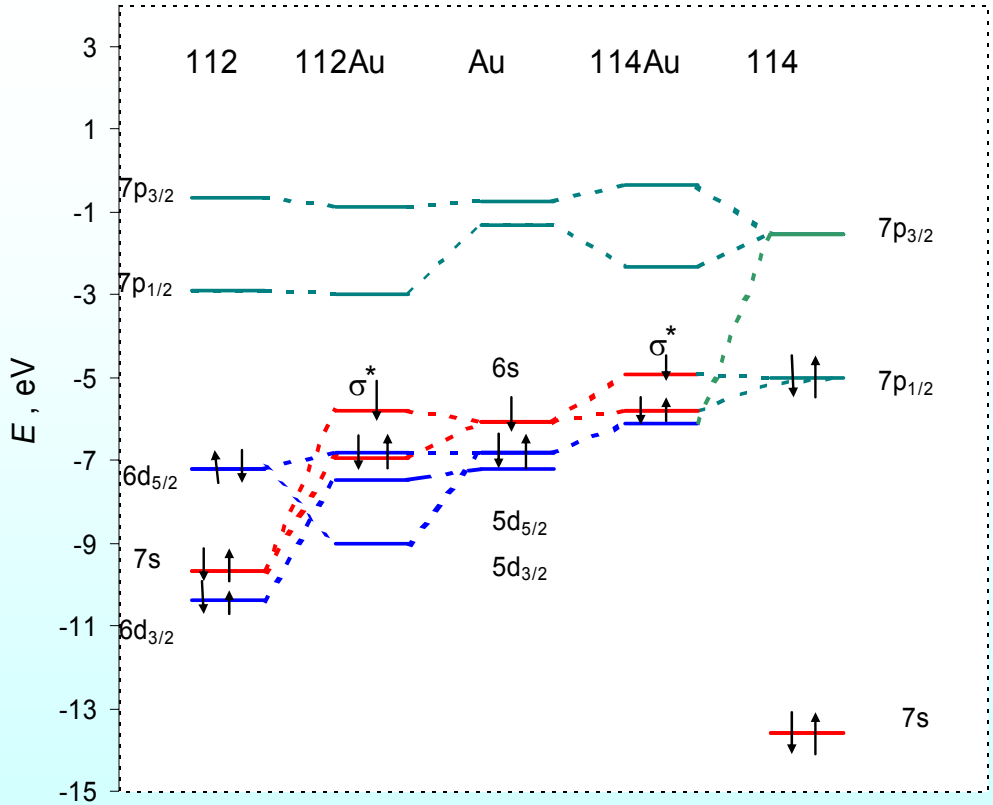


Bond Formation in CnAu and 114Au

Cn/Au

ΔE[7s(Cn)-6s(Au)] = -4.33 eV

D_e = 0.51 eV

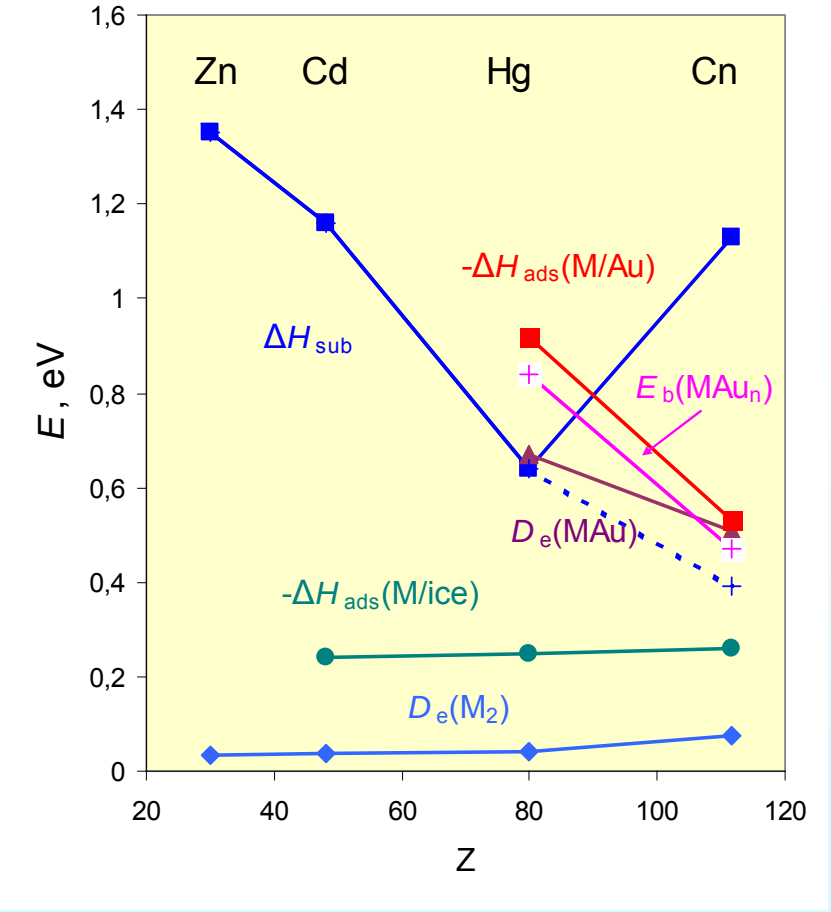


114/Au

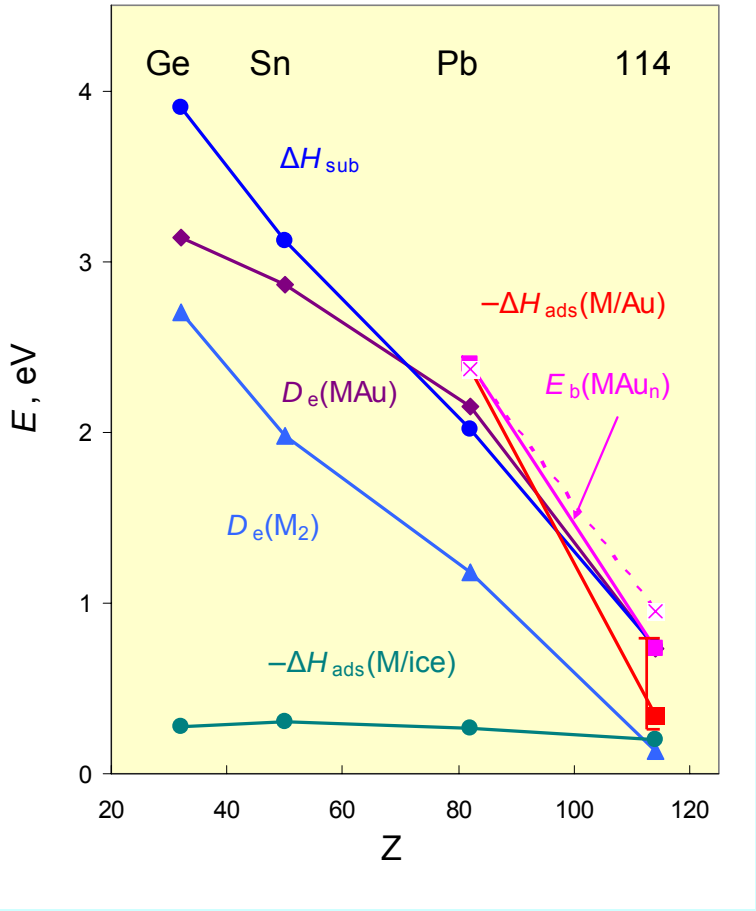
ΔE[$7p_{1/2}$(114)-6s(Au)] = 1.74 eV

D_e = 0.73 eV

Summary of Group 12 and 14 Binding Properties

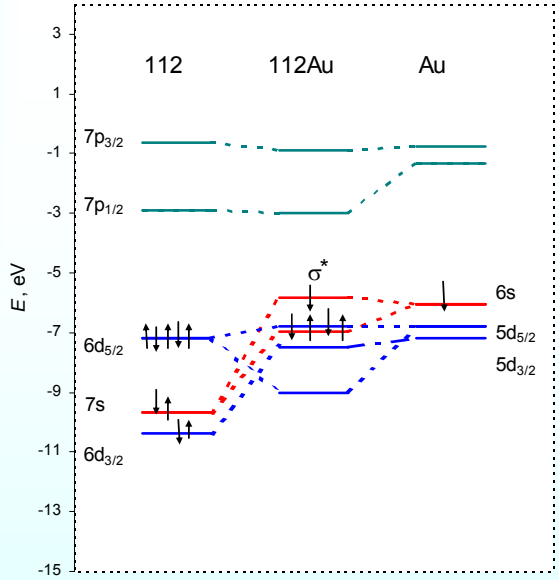


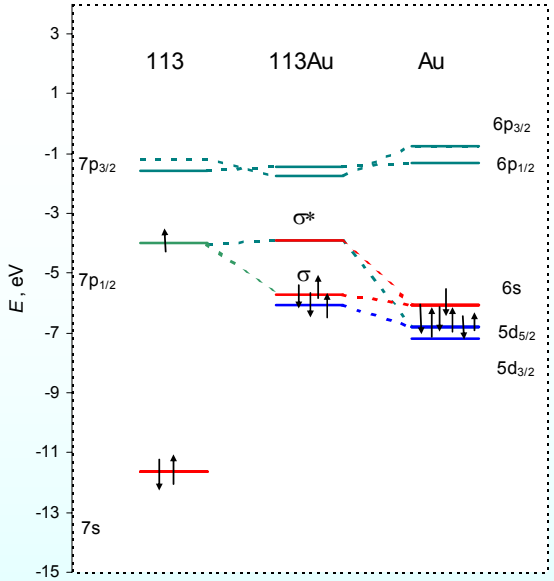
$\Delta H_{sub}(M) \neq k\Delta H_{ads}(M)/Au$

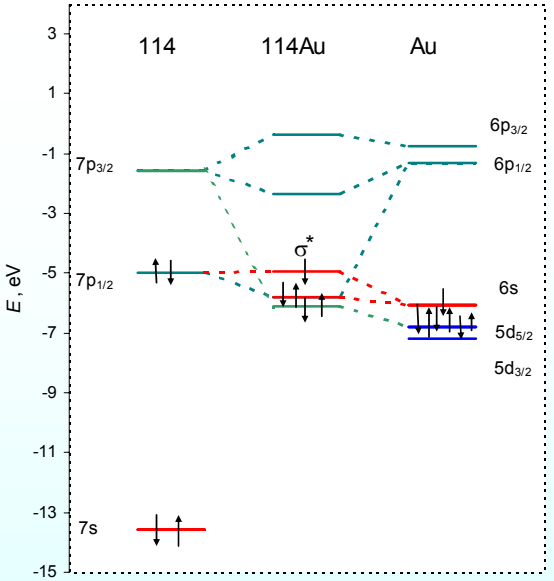


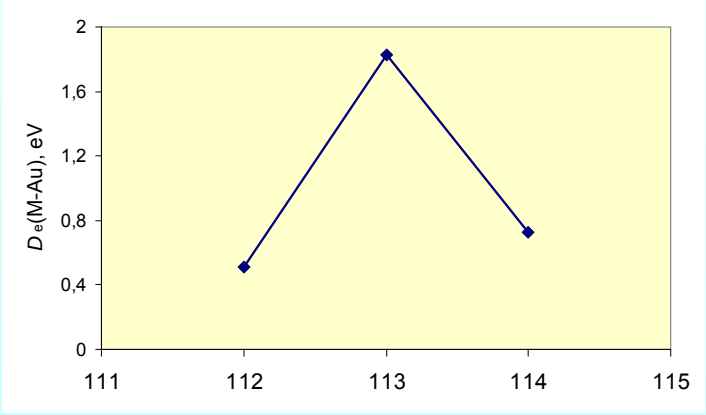
[V. Pershina, Radiochim. Acta 99, 459 (2011)]

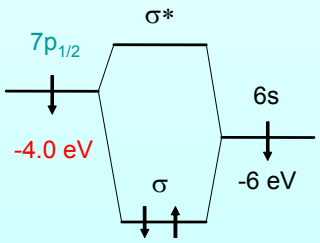
M-Au Bonding (M = 112, 113 and 114)



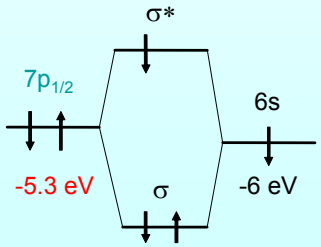








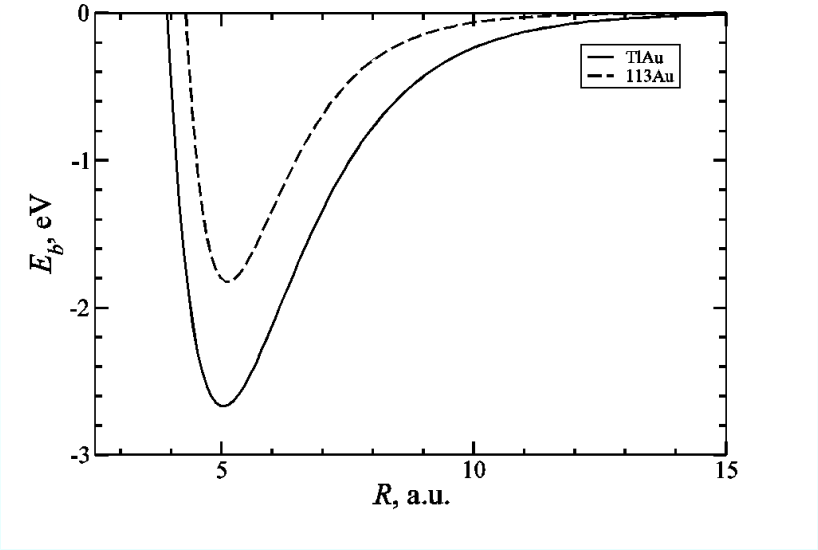
1.83



0.73 eV

Interaction of Element 113 with Gold

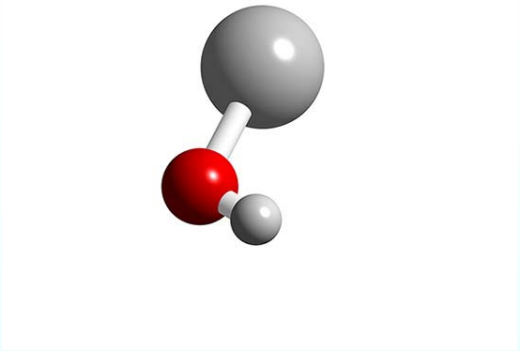
Potential energy curves for TlAu and 113Au:



Method	TlAu		113Au		ΔD_e
	R_e, Å	D_e, eV	R_e, Å	D_e, eV	ΔD_e
4c DFT/B88/P86	2.67	2.67	2.72	1.83	0.84
2c DFT/PBE0	2.65	2.24	2.69	1.38	0.86
2c DFT B3LYP	2.70	2.24	2.72	1.31	0.93
1c CCSD(T) + ΔSO	2.62	2.41	2.66	1.57	0.84

4c-DFT – our; 2c-RDFT, 1c-CCSD(T) – van Wüllen and Zaitsevskii.

MAu and MOH (M = Tl and 113)



M-OH

Bond lengths (R_e), dissociation energies (D_e), vibrational frequencies (w_e), dipole moments (μ), polarizabilities (α), and ionization potentials (IP)

Molecule	R_e, Å	D_e, eV	w_e, cm^{-1}	μ, D	α, a.u.	IP, eV
TlAu	2.69	2.67	141	0.49	76.43	5.480
113Au	2.72	1.83	144	0.33	75.27	8.532
TlOH	2.19	3.68	547	0.47	45.7	9.262
113OH	2.29	2.42	519	0.45	41.6	9.581

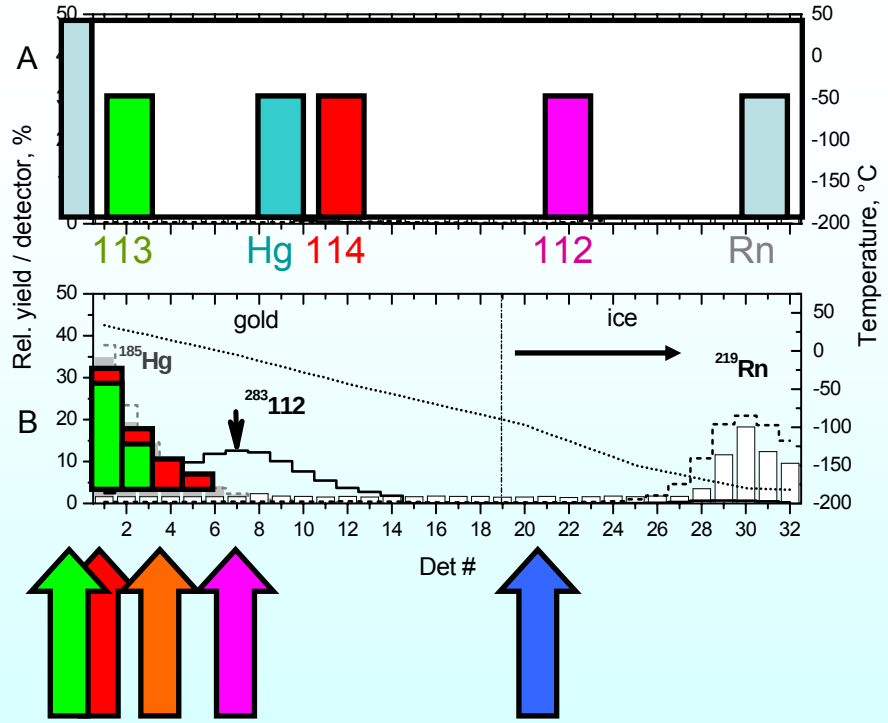
$$E(x) = -\frac{\alpha_{mol}}{8\left(\frac{1}{IP_{Au}} + \frac{1}{IP_{mol}}\right)x^3}$$

$-\Delta H_{ads}$ of M and MOH on Au

	$-\Delta H_{ads}$, 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	86	on Au	this

[V. Pershina, *et al*. Chem. Phys. Lett. 480, 157 (2009)]

Predictions of Adsorption Behaviour of Elements 112, 113 and 114



113 114 112

114 exp.-2

114 exp.-1

112

Theory: $-\Delta H_{ads}$(calc.) = 46 kJ/mol

[V. Pershina *et al*., JCP 2009]

Exp.: T_{ads}(exp.) = -5 °C

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

114

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

Exp.-1 T_{ads} = - 88 °C

$-\Delta H_{ads}$ = 34^{+54}_{-11} kJ/mol

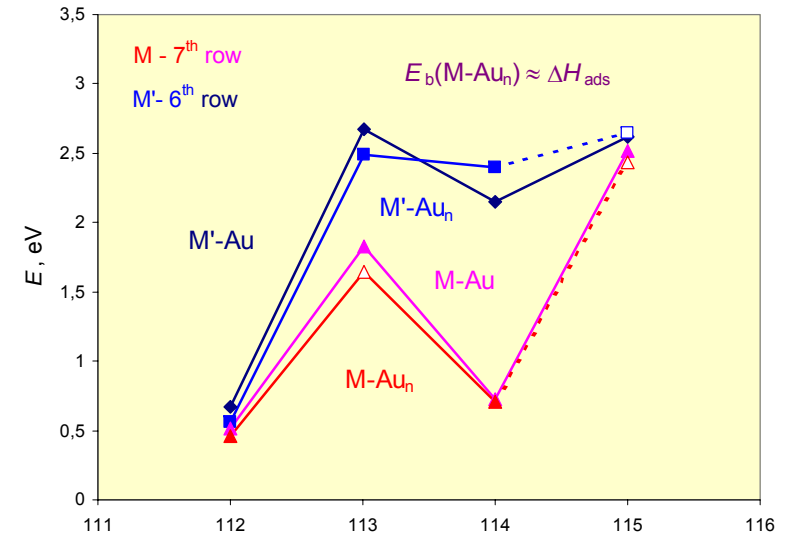
[R. Eichler, *et al*. Radiochim. Acta, 2009]

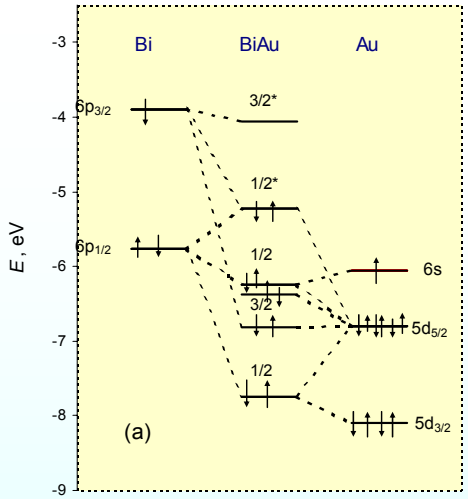
Exp.-2 T_{ads} = + 25 °C

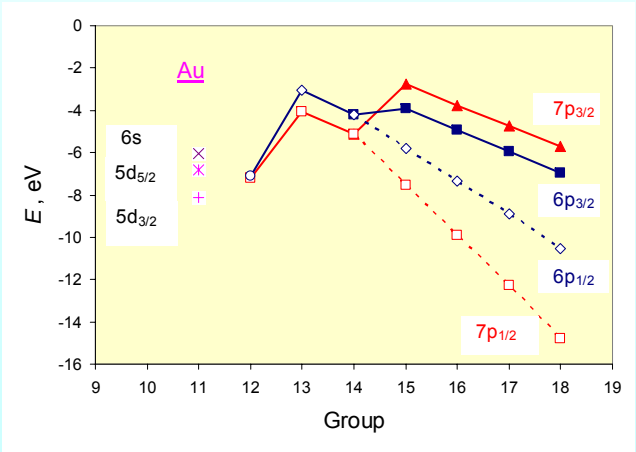
$-\Delta H_{ads}$(114) ≥ Cn

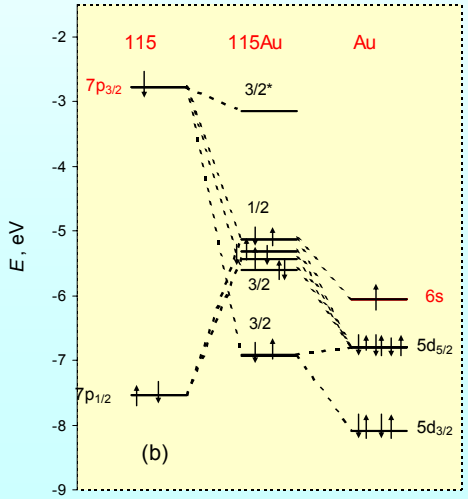
[A. Yakushev, to be published]

Adsorption of Z > 114 on Gold

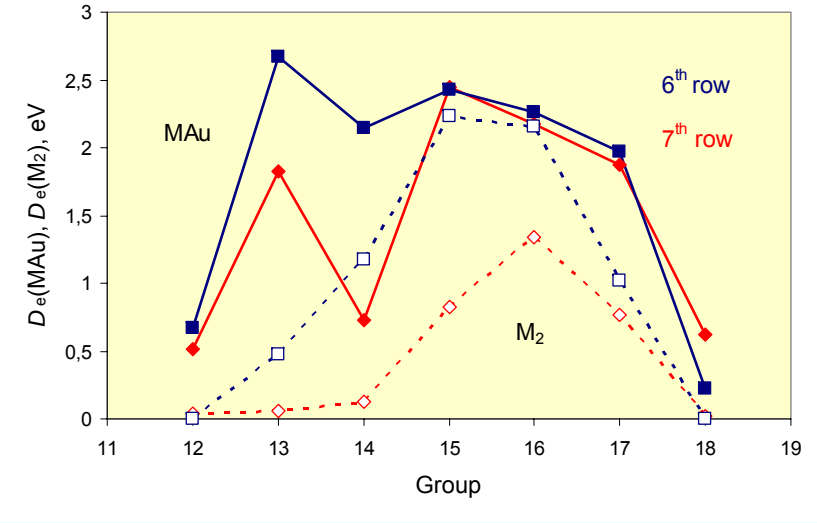


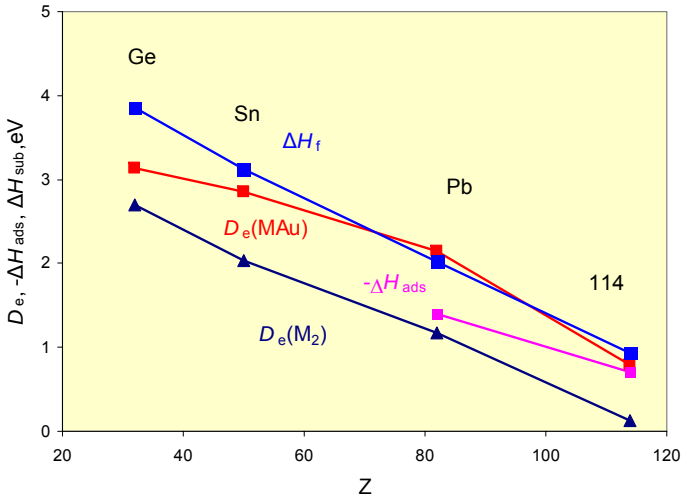


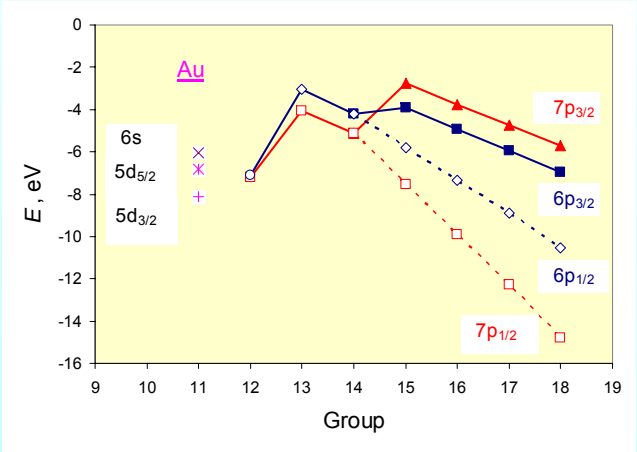


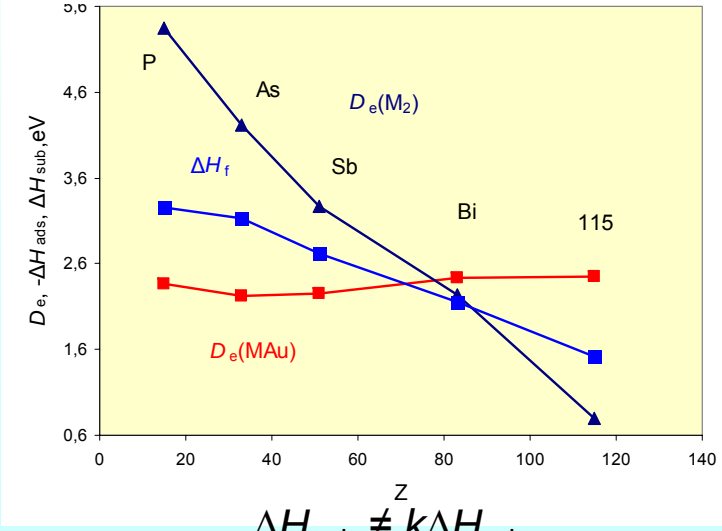


Different Trends in M-M and M-Au Binding





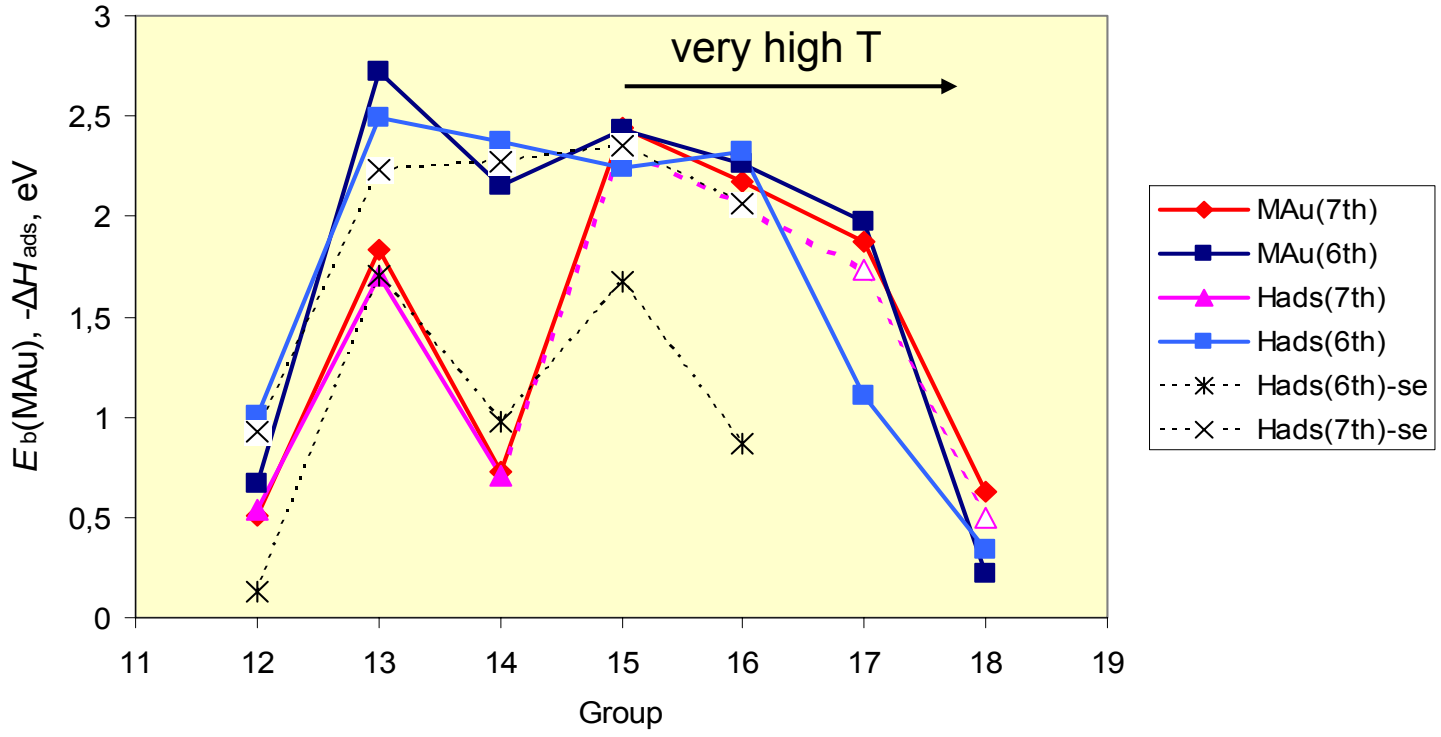




[V. Pershina, *et al*. J. Chem. Phys. 133, 104304 (2010)]

$\Delta H_{sub} \neq k\Delta H_{ads}$

Adsorption of 6th and 7th Row Elements on Gold

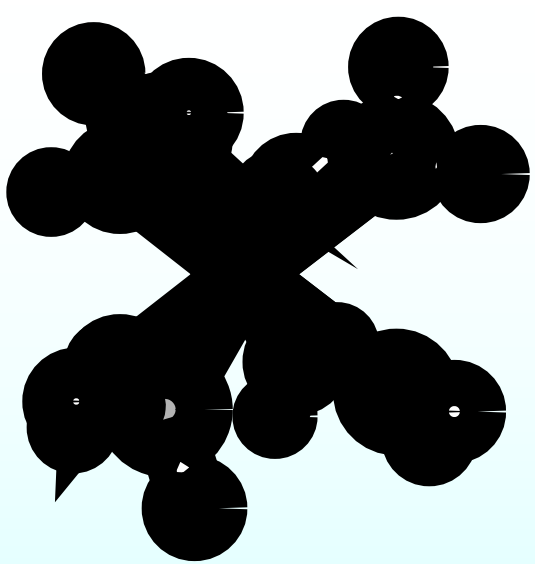


Summary of Aqueous Chemistry Studies

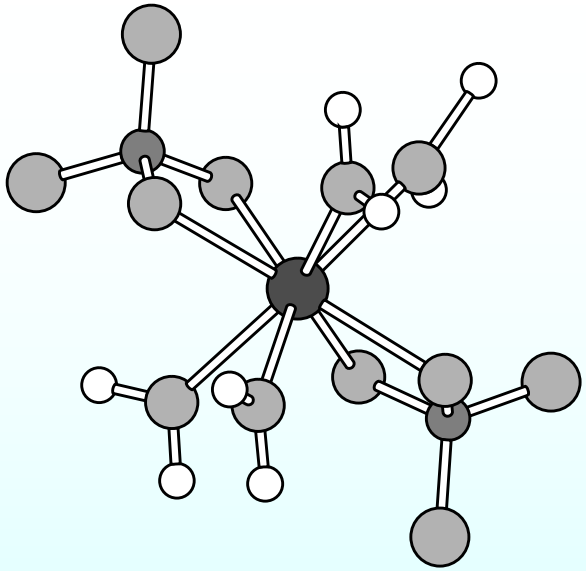
Trends in the complex formation

Group	Complexes	Theoretically predicted	Author (Pershina)	Experimentally observed	Author
4	Hydrolysis of M^{4+}	Zr > Hf > Rf	2002	Zr > Hf > Rf	Czerwinski 1992
	$MF_x(H_2O)^{z-x}_{8-x}$ ($x \leq 4$)	Zr > Hf > Rf	2002	Zr > Hf > Rf	Strub 2000, Ishii 2008
	MF_6^{2-}	Rf ≥ Zr > Hf	2002	Rf ≥ Zr > Hf	Trubert 1999
	MCl_6^{2-}	Zr > Hf > Rf	2002	Rf > Zr > Hf	Haba 2002
	$M(SO_4)_4^{4-}$	Zr > Hf >> Rf	2006	Zr > Hf >> Rf	Omtwedt, Li 2011
5	Hydrolysis of M^{5+}	Nb > Ta > Db	1998	Nb > Ta	Czerwinski 1992
	$MOCl_4^-$, MCl_6^-,	Pa >> Nb ≥ Db > Ta	1998	Pa >> Nb ≥ Db >Ta	Paulus 1999
	MF_6^-, MBr_6^-	Nb > Db > Ta	1999	Nb > Db > Ta	Paulus 1999
!	Hydrolysis of M^{6+}	Mo > W > Sg	2001	Mo > W > Sg	Schädel 1998
	Hydr. of $MO_2(OH)_2$	Mo > Sg > W	2001	Mo > W ?? Sg	Schädel 1998
	$MO_2F_2(H_2O)_2$	Mo > Sg > W	2004	Mo > W ?? Sg	Kronenberg 2004
	MOF_5^-	Mo < W < Sg	2004	Mo < W ?? Sg	Kronenberg 2004
8	$MO_4(OH)_2^{2-}$	Os > Hs >> Ru	2005	Os ≥ Hs	von Zweidorf 2004
				Os > Ru	Samadani 2010

Complexes of Zr, Hf and Rf in H_2SO_4



$M(H_2O)_8^{4+}$



$M(SO_4)_2(H_2O)_4$

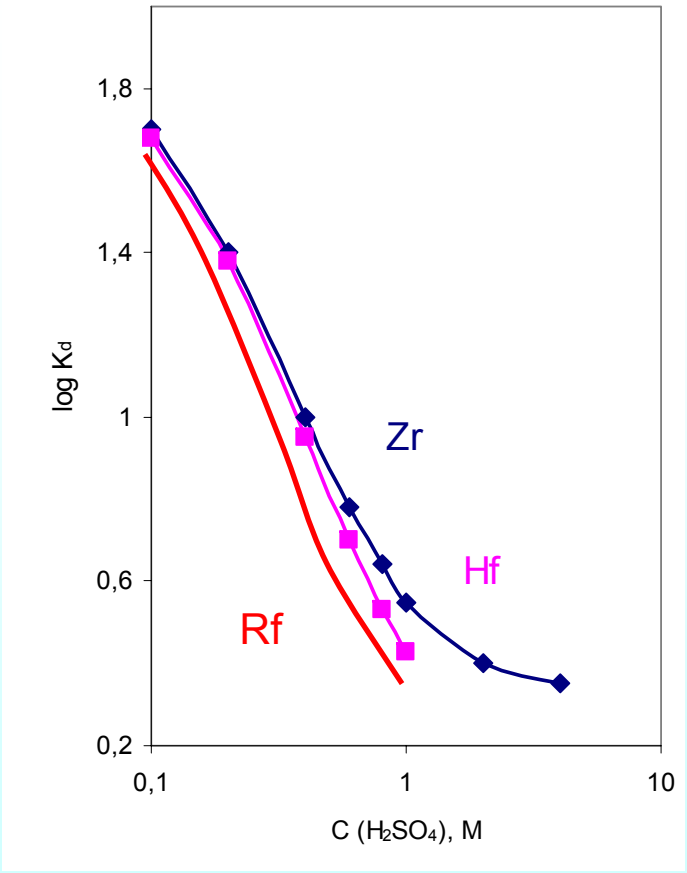
Complex formation reactions:

$$M(H_2O)_8^{4+} \Leftrightarrow M(SO_4)_2(H_2O)_4 \Leftrightarrow M(SO_4)_3(H_2O)_2^{2-} \Leftrightarrow M(SO_4)_4^{4-}$$

$$MOH(H_2O)_7^{3+} \Leftrightarrow M(SO_4)_2(H_2O)_4 \Leftrightarrow M(SO_4)_3(H_2O)_2^{2-} \Leftrightarrow M(SO_4)_4^{4-}$$

Prediction of K_d for Hf and Rf

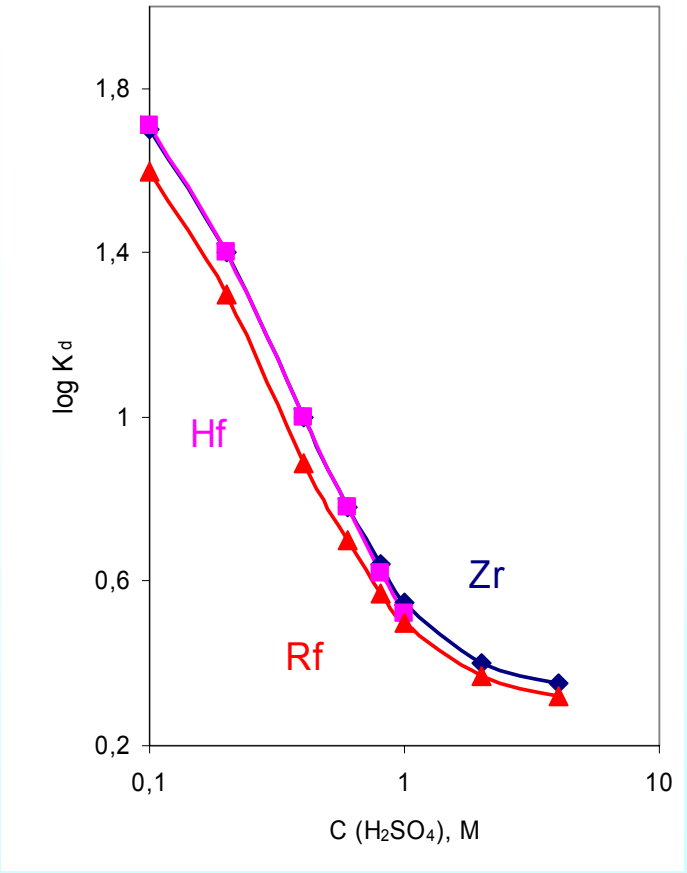
experiment



Zr > Hf > Rf

[D. Polakova, *et al.* RA 2007, J Li, RA 2011]

theory



Zr ≥ Hf > Rf

[V. Pershina, *et al*. RA 2006]

Prospects

- Methodical developments
  - Atomic
    - QED effects on the SCF basis
    - Open-shell correlated methods (FSCC, MSCC)
  - Molecular
    - *ab initio* DCB correlated for chemically interesting cases
      - basis sets, correlation techniques
    - *ab initio* predictions of (molecular, adsorption) properties
- New systems
  - new elements: Mt, Ds...
  - new compounds: metallo-organic, *etc*.