SHE Theoretical Chemistry

V. Pershina

GSI, Darmstadt, Germany

Aim of Chemical Research on SHEs

- To place elements in the Periodic Table
- Study chemical properties
- Study relativistic effects influence

Properties needed to Place new Elements in the Periodic Table

- Fundamental properties
  - Atomic number (Z≤113)
    (Z≥113)
  - Electronic configuration

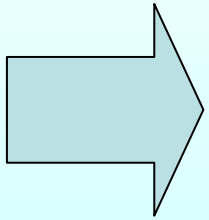
Experimental:

α-decay

not : SF

cannot be measured

- Chemical properties
  - Ionic radii
  - Stable oxidation states
  - Complex formation



Indirect

by comparison

with homologs

Chemical Properties

Experiment

- Reduction (aqueous)
  - E° (M^{z+})
- Liquid chromatography
  - $K_d \rightarrow \Delta H_{c.f.}$
- Gas-phase chromatogr.:
  - T_{ads} (models $\rightarrow \Delta H_{ads}$)

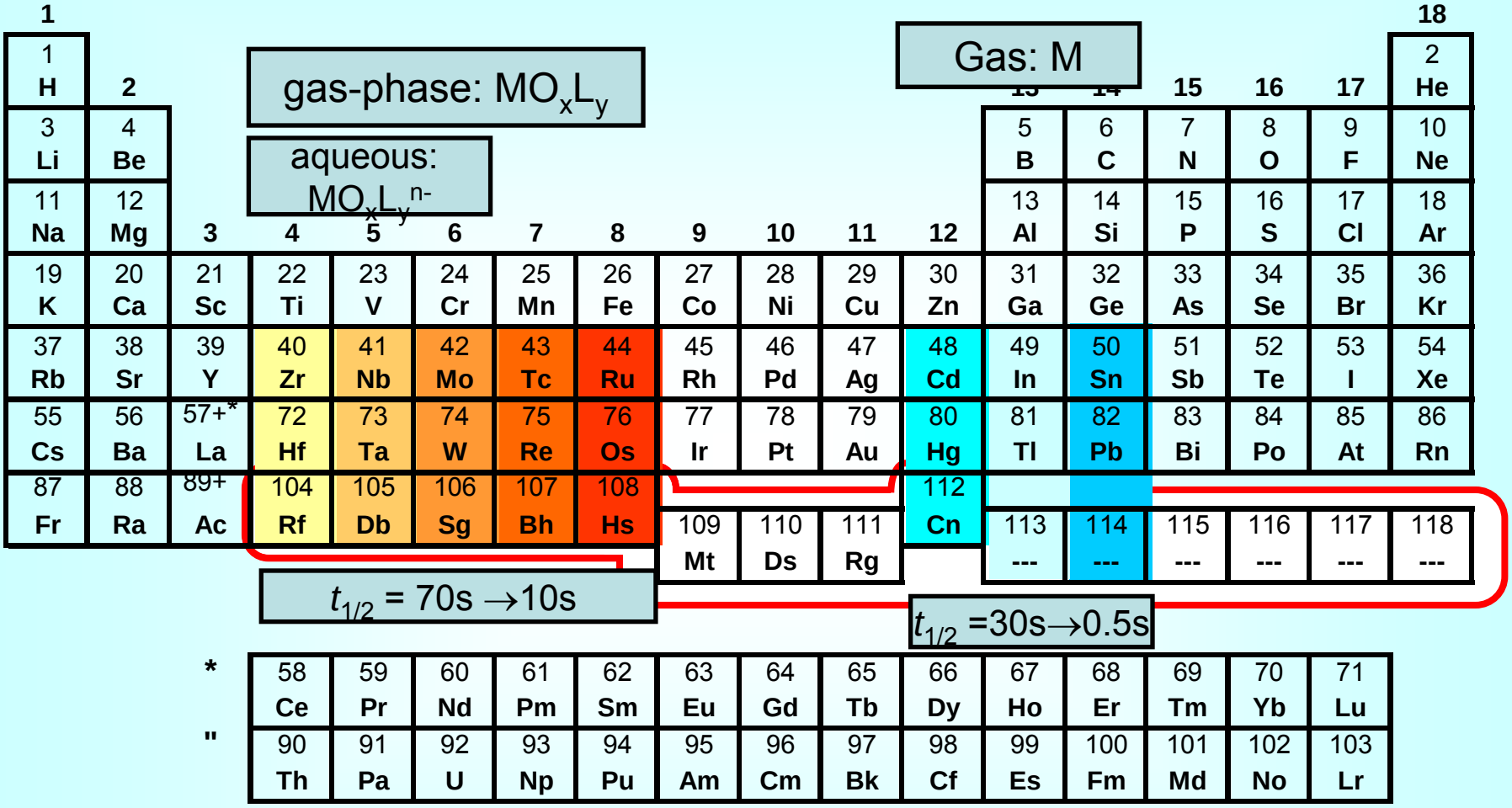
Chemical composition is not known!

Theory

Important!

- Direct
  - Electronic configurations
  - Atomic:
    - IP, EA, α, E
    - ΔH_{ads}
  - Molecular:
    - chem. comp., D_e, R_e, IR
    - IP, EA, EE, k, α, μ
    - ΔH_{ads}, $\Delta H_{c.f.}$
- Models
  - K_d, E°, T_{ads}
- Relativistic effects!!!

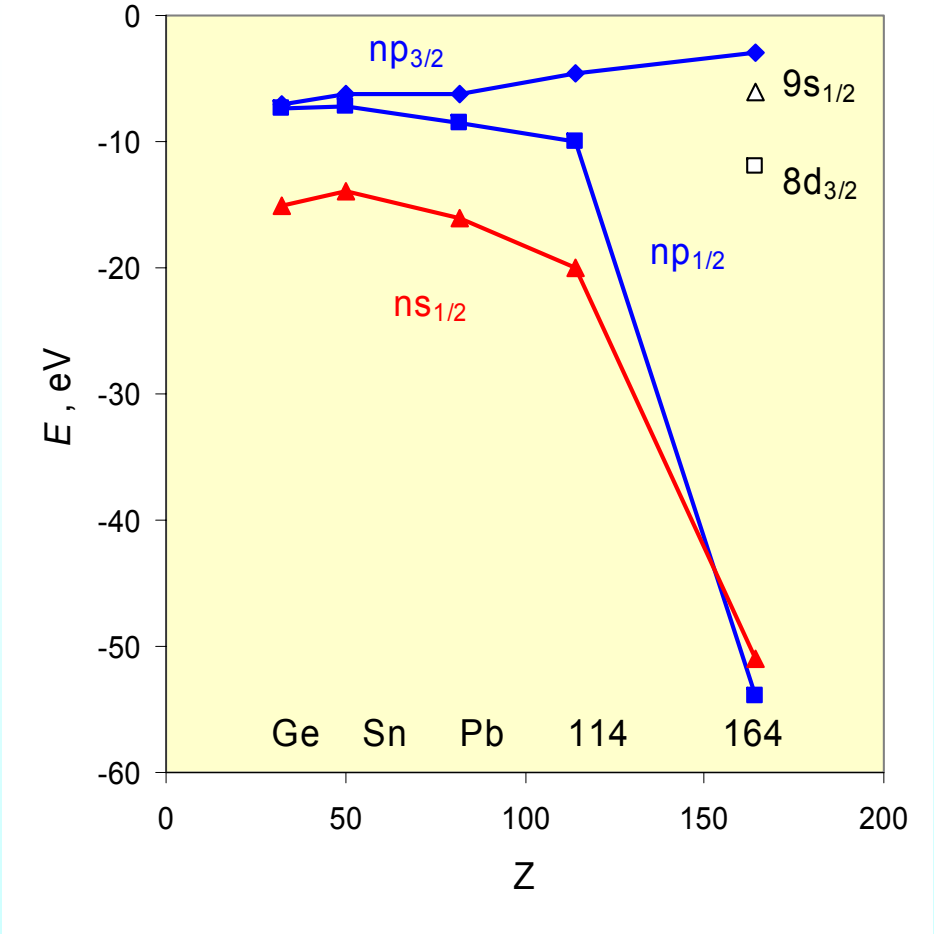
Chemically Studied Systems of SHEs



	1																	18
	1 H	2											13	14	15	16	17	2 He
	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
	11 Na	12 Mg	3	4	5	6	7	8	9	10	11	12	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
	55 Cs	56 Ba	57+* La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
	87 Fr	88 Ra	89+ Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 ---	114 ---	115 ---	116 ---	117 ---	118 ---

*	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
"	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Relativistic Effects in Group 14



[B. Fricke, Struct. Bond **21**, 89 (1975)]

Modern Hamiltonian

- Dirac-Coulomb-Breit

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

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

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

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

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

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

- QED effects
  - perturbatively

Relativistic Methods used for SHE Atoms

- DC(B) (meV accuracy)
  - CCSD(T), FSCC, IHFSCC... (Tel Aviv code, DIRAC)
  - QED
    - Perturbation Theory
- MCDF (~0.1 eV)
  - Desclaux /Indelicato/Fricke (Breit-SCF, QED-PT)
  - Nefedov
- DF (Desclaux/Fricke)
- DFT+QED (Saito)

Systems

- M: 103, 104, 111-122
  - EA(118)
  - IP (< 1%): 111-113, 118-120
- M, M^{z+}: 103-108, 112, 114, 117
- M^{Z+}: 119-121 ... 168
- M: 119-164
- M: 104-172
- M: 121-131

Relativistic Molecular Methods for SHE

- *ab initio* DF/DC (CI, MP2,CCSD) (DIRAC)
- ECP
  - RECP + CCSD(T) (USA, Korea)
  - PP + CCSD(T) (Stuttgart)
- RDFT
  - 4*c*-DFT (Kassel, Ulm)
  - 4*c*-BDF (China)
  - 2*c*-DFT (ADF)
- Solid state DFT

- 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

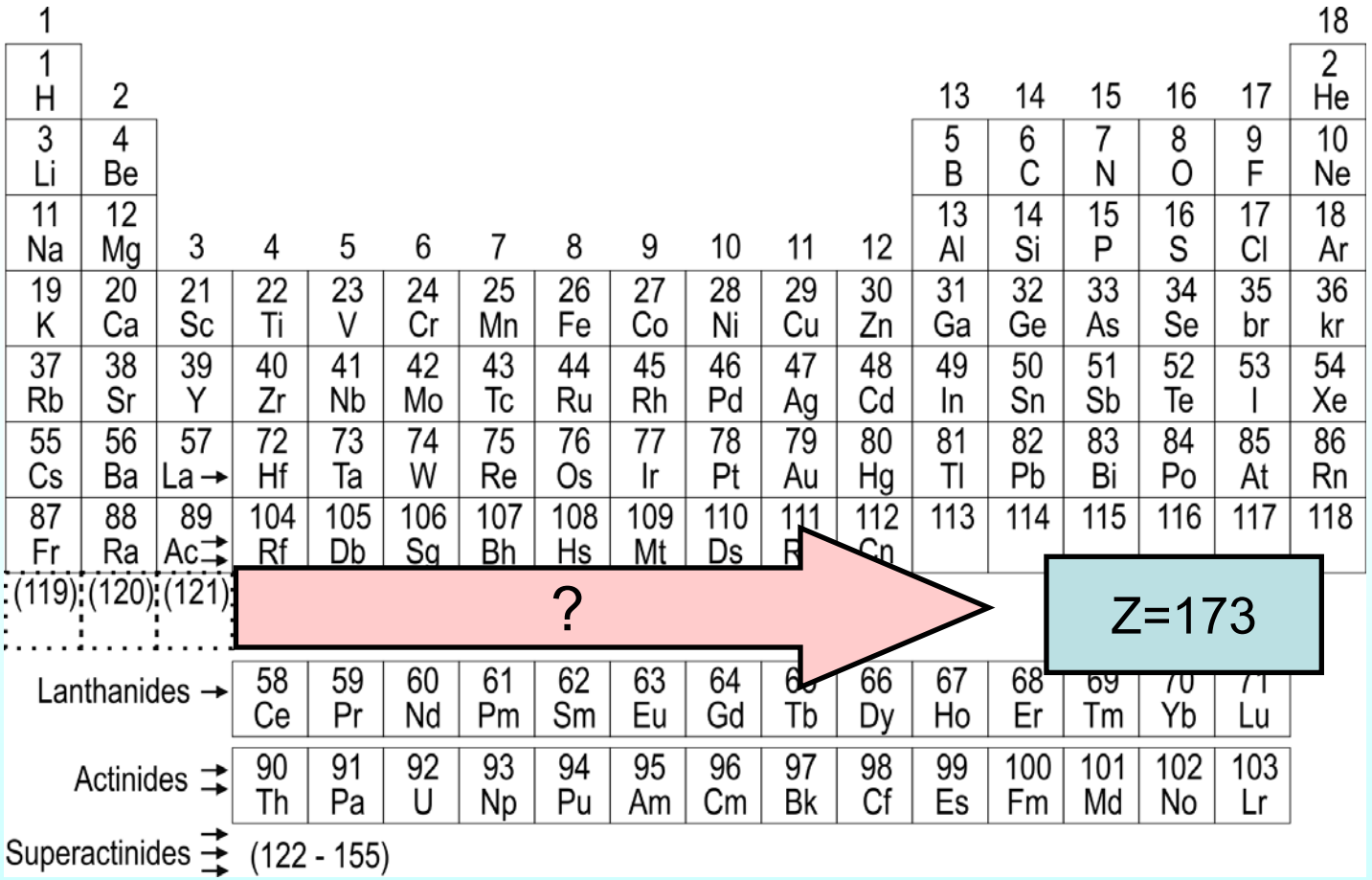
No highly accurate FSCC calculations for Z > 122

MCDF(OL) are restricted due to computer limitations

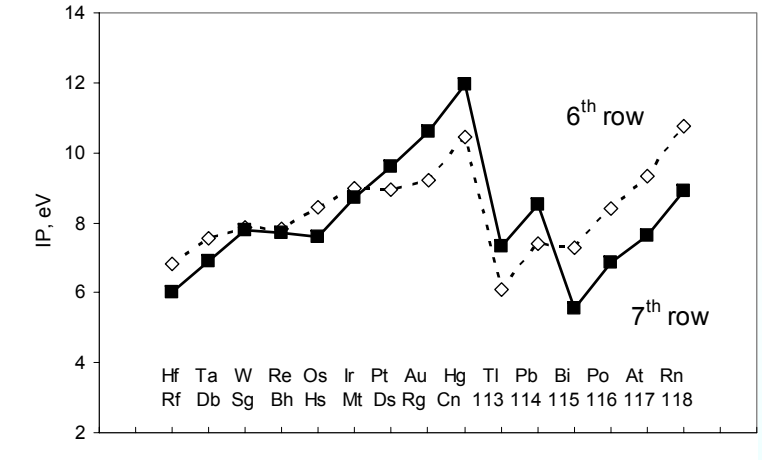
MCDF + Breit + QED: confirmed the end of the PT with Z = 173 [$E(1s) < -2mc^{2}$]

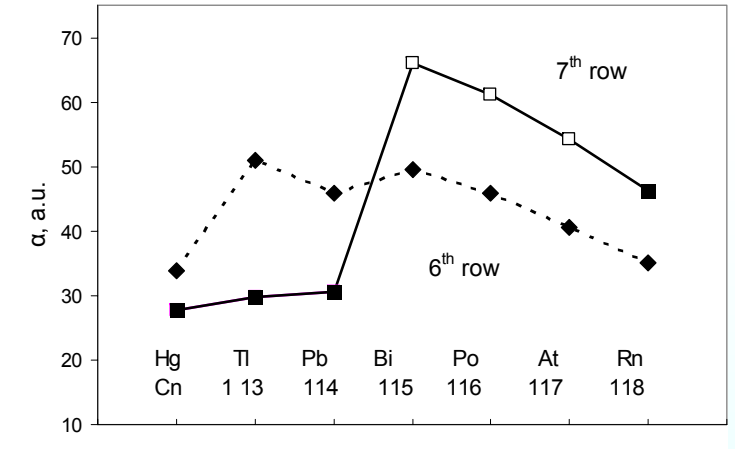
[P. Indelicato, Theor. Chem. Acc. 129, 495 (2011)]

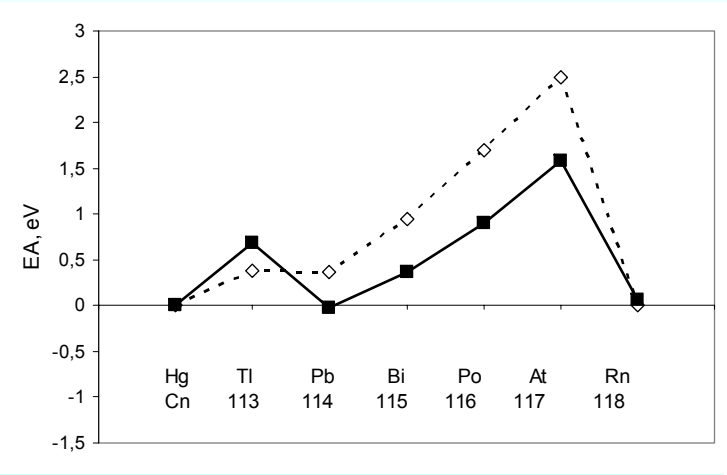
Modern Periodic Table of Elements

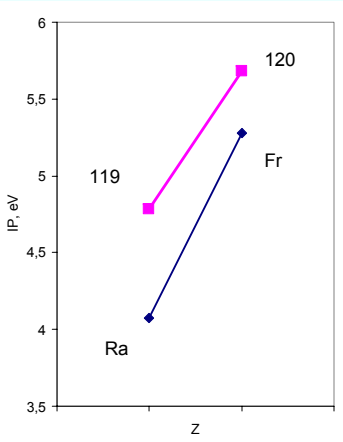


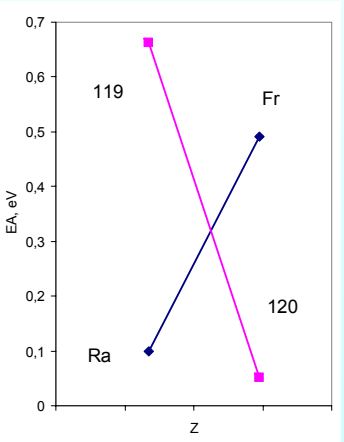
Systematics of SHE Atomic Properties

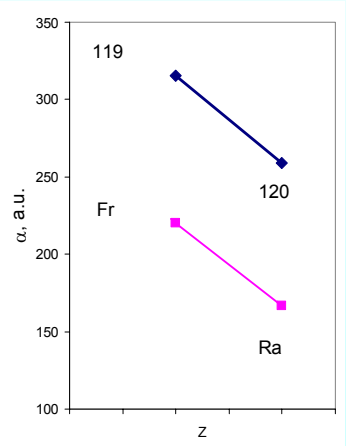








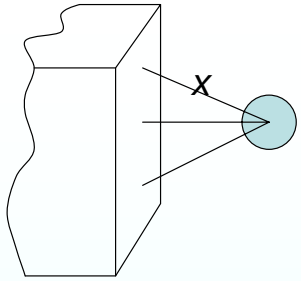




Predictions of Adsorption on Inert Surfaces

An atom-slab model:

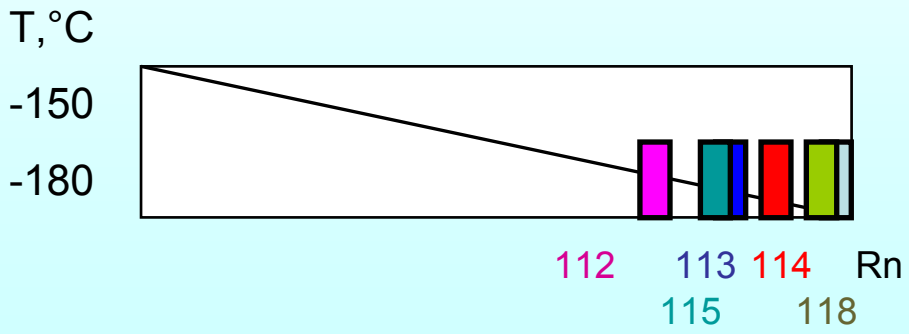
$$E(x) = -\frac{3}{16}\left(\frac{\varepsilon - 1}{\varepsilon + 2}\right)\frac{\alpha_{mol}}{\left(\frac{1}{IP_{slab}} + \frac{1}{IP_{at}}\right)x^3}$$



DC(B) calculations of IP, α, etc.

Property	112	113	114	115	...	118	Rn
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

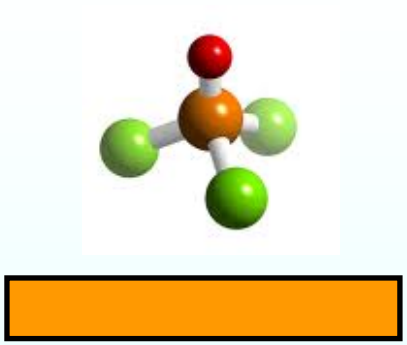


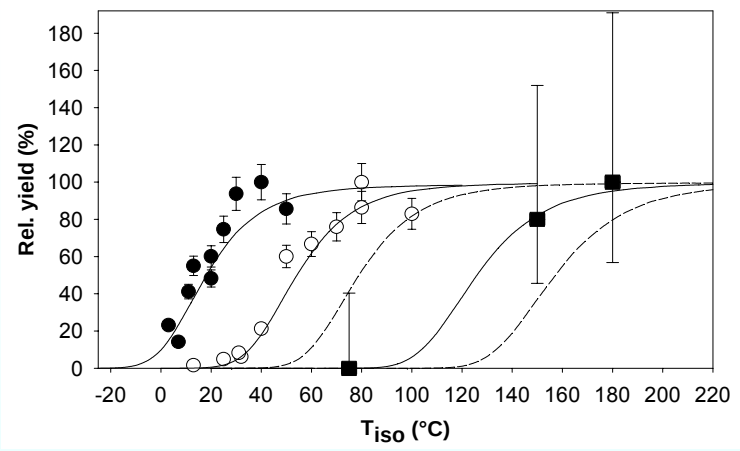
Stable Molecules and their Properties

Group	Molecule	R_e, Å	D_e, eV	IP, eV	μ, D	α, a.u.
4	$ZrCl_4$	2.34	21.68	-	-	-
	$HfCl_4$	2.34	21.14	-	-	-
	$RfCl_4$	2.40	19.50	10.96	-	-
5	$NbCl_5$	2.43/2.24	*19.25*	10.77	-	-
	$TaCl_5$	2.37/2.23	*19.46*	10.73	-	-
	$DbCl_5$	2.42/2.28	17.76	10.83	-	-
	$NbOCl_3$	1.66/2.24	*21.6*	11.60	0.91	-
	$TaOCl_3$	1.67/2.25	*22.52*	11.57	0.99	-
	$DbOCl_3$	1.72/2.30	20.82	11.64	1.27	-
	$NbBr_5$	2.50/2.45	18.32	9.35	-	172.1
	$TaBr_5$	2.49/2.44	19.41	9.33	-	167.3
	$DbBr_5$	2.55/2.50	18.86	9.37	-	167.0
	$NbOBr_3$	1.70/2.44	20.53	-	-	-
	$TaOBr_3$	1.72/2.44	21.43	-	-	-
	$DbOBr_3$	1.79/2.48	20.36	-	-	-
6	$MoCl_6$	2.25	-	11.06	-	-
	WCl_6	2.26	*21.7*	11.13	-	-
	$SgCl_6$	2.32	20.05	11.17	-	-
	$MoOCl_4$	1.66/2.28	*20.54*	-	0.14	-
	$WOCl_4$	1.69/2.28	*22.96*	-	0.49	-
	$SgOCl_4$	1.75/2.34	*21.24*	-	1.03	-
	MoO_2Cl_2	1.69/2.26	*21.08*	-	1.04	-
	WO_2Cl_2	1.71/2.27	*23.5*	-	1.35	-
	SgO_2Cl_2	1.77/2.33	21.6	-	1.83	-
	WO_3	1.74	18.9	-	-	-
	SgO_3	1.78	17.8	-	-	-
7	TcO_3Cl	1.69/2.30	23.12	12.25	0.93	33.33
	ReO_3Cl	1.71/2.28	24.30	12.71	1.29	39.88
	BhO_3Cl	1.77/2.37	22.30	13.05	1.95	50.61
8	RuO_4	1.71	27.48	12.21	-	58.07
	OsO_4	1.72	27.71	12.35	-	55.28
	HsO_4	1.80	28.44	12.29	-	68.88

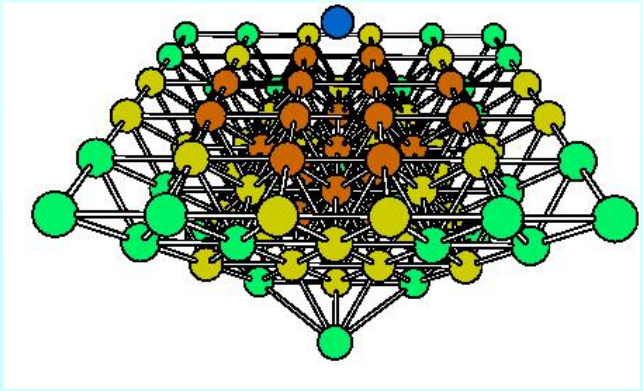
Adsorption on Surfaces

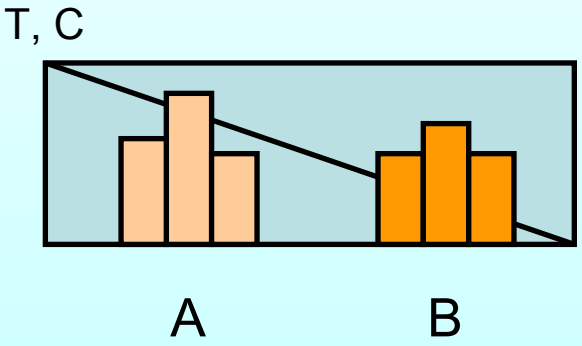
- Inert surfaces





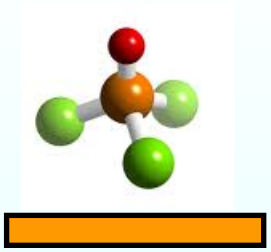
- Metal surfaces





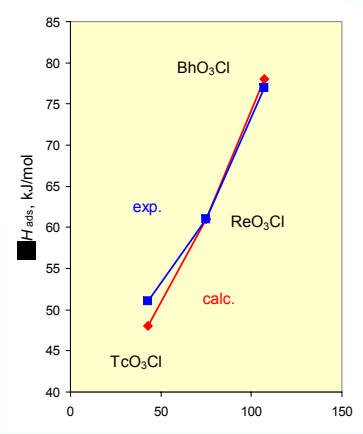
Adsorption of Oxyhalides

- Group 7
  - MO_3Cl

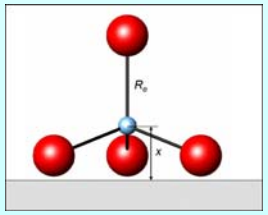


$$E(x) = -\frac{2Qe\mu_{mol}^{\ 2}}{x^2} - \frac{Q^2e^2\alpha_{mol}}{2x^4} - \frac{3}{2}\frac{\alpha_{mol}\alpha_{Cl}}{\left(\frac{1}{IP_{mol}} + \frac{1}{IP_{Cl}}\right)x^6}$$

	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

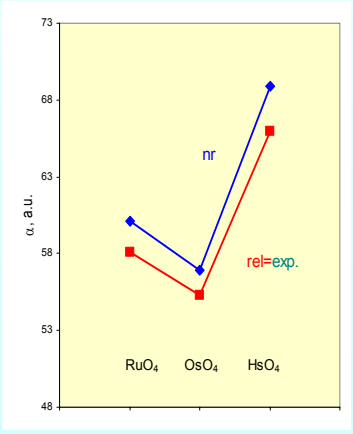


- Group 8
  - MO_4

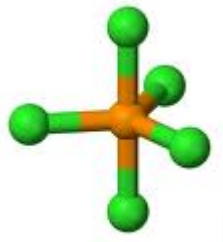


$$E(x) = -\frac{3}{16}\left(\frac{\varepsilon - 1}{\varepsilon + 2}\right)\frac{\alpha_{mol}}{\left(\frac{1}{IP_{slab}} + \frac{1}{IP_{mol}}\right)x^3}$$

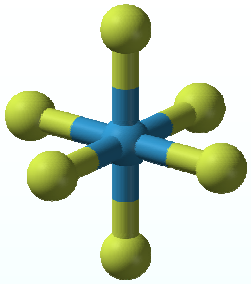
Property	RuO_4	OsO_4	HsO_4	Ref.
α, a.u.	58.07	55.28	66.00	calc.
$-\Delta H_{ads}$ (kJ/mol) calc.	40.23	39.0	46.5	calc.
$-\Delta H_{ads}$ (kJ/mol) exp.	-	39 ± 1	46 ± 2	exp.



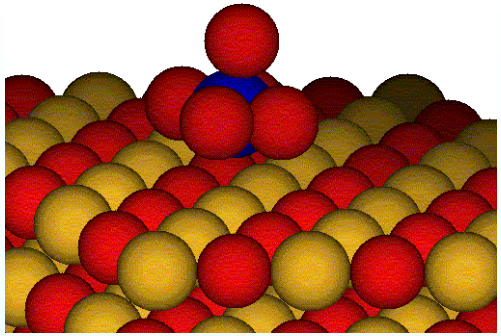
Salt Formation on Surface

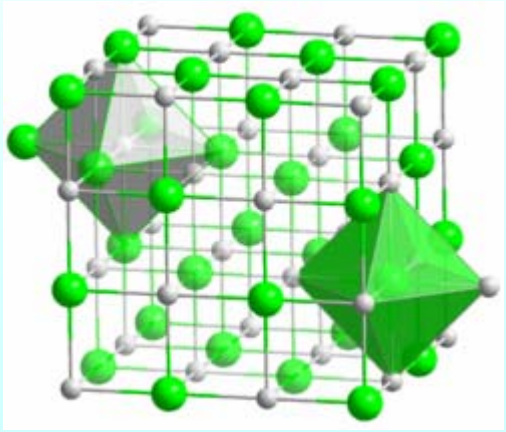


MBr_5 + Br^- ⟹



MBr_6^-



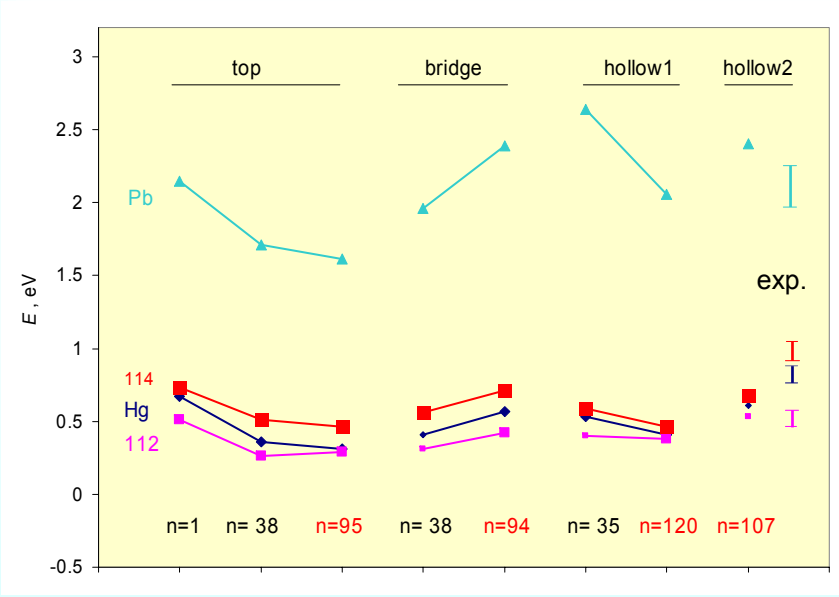


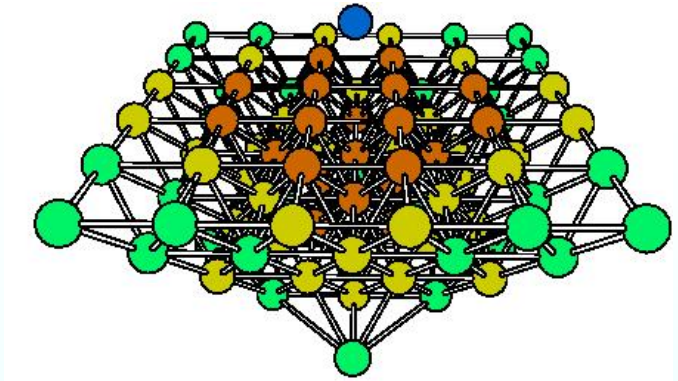
KBr

Molecule	Nb	Ta	Db	Trend in vol.
$\Delta\Delta E^r(MBr_5 \rightarrow MBr_6^-)$ / Nb	0	-0.09	-0.21	Nb > Ta > Db
$-\Delta H_{ads}(SiO_2/KBr)$ / Nb [Tűrler]	0	-0.08	-0.29	Nb > Ta > Db
$-\Delta H_{ads}(SiO_2/KBr)$/ Nb [Q Zhi]	0	-0.08	+0.18	Nb > Ta < Db

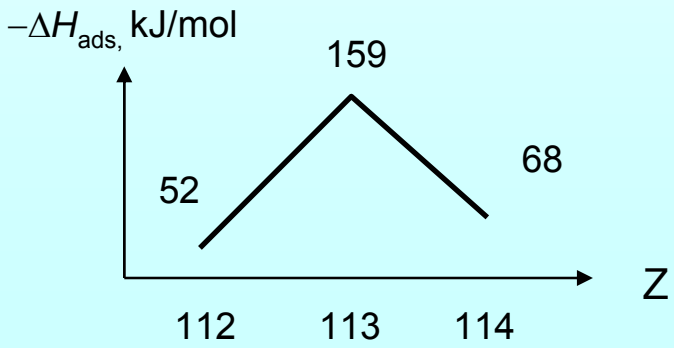
Adsorption on Gold

M-Au$_n$ binding energies



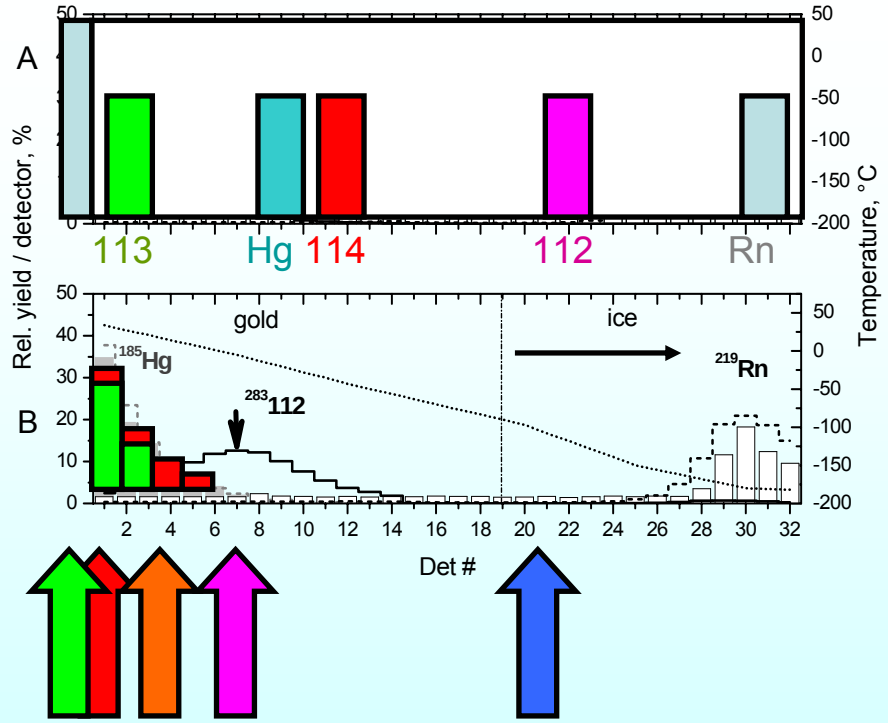


M	position, n	E_b, eV	ΔH_{ads}, eV	Ref. (exp.)
Hg	bridge n=94	**0.56**	**0.92**	B. Eichler
Cn	hollow n=107	**0.46**	**$0.54^{+0.4}_{-0.03}$**	R. Eichler
Pb	bridge n=94	**2.40**	**2.43**	Haennsler
114	bridge n=94	**0.71**	**$0.36^{+0.5}_{-0.1}$**	R. Eichler
			≥ 0.54	A. Yakushev
Tl	top n=1	**2.65**	**2.48**	Serov
113	top n=1	**1.34**	**(1.65)**	-



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

Prediction of Adsorption Behaviour of Elements 112, 113 and 114 on Gold



113 114 112

114 exp.-1

114 exp.-2

112

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

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

114

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

Exp.-1 $-\Delta H_{ads} = 34^{+54}_{-11}$ kJ/mol

[R. Eichler]

Exp.-2 T_{ads} = + 25 °C

$-\Delta H_{ads}$(114) ≥ Cn

[A. Yakushev]

Solid State DFT Calculations

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

    [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)

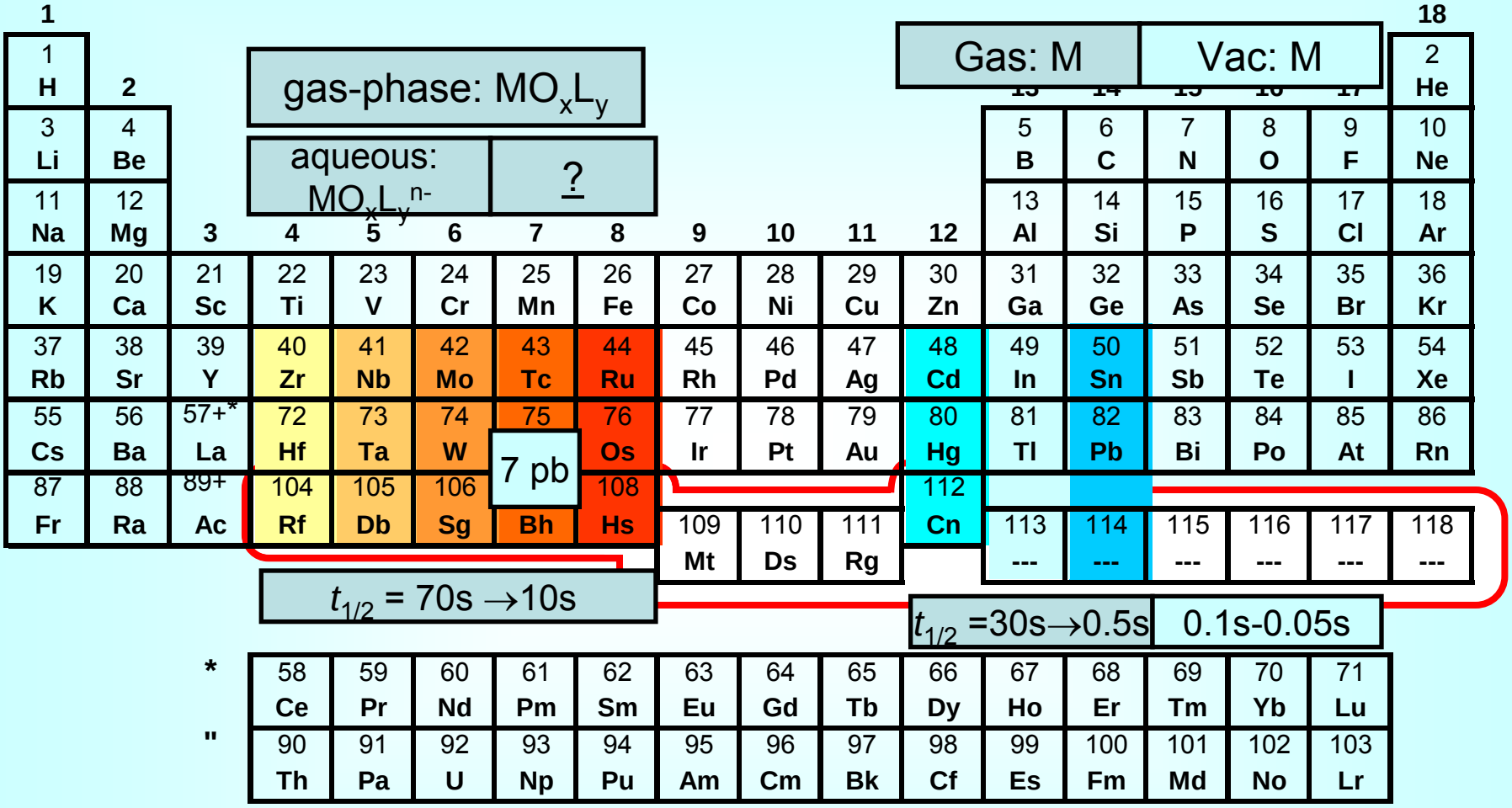
    [A. Hermann, *et al*. Phys. Rev. B 82, 155116 (2010)]

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

Summary of Gas-Phase Adsorption Studies

Group	Compounds	Theoretically predicted volatility	Experimentally observed volatility	Problem solved
4	MCl_4, MBr_4	Hf < Rf	Zr > Hf < Rf	not
5	MCl_5	Nb < Ta < Db	Ta > Db ($DbOCl_3$)	not
	MBr_5 (MBr_6^-)	Nb > Ta > Db	Nb > Ta > Db	yes
			Nb > Ta < Db	not
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
12	M/Au	Hg < Cn	Hg < Cn	yes
13	M/Au	Tl < 113	Tl	not
14	M/Au	114 < Cn	114 > Cn; 114 < Cn	not

Prospects for Chemical Studies of SHEs

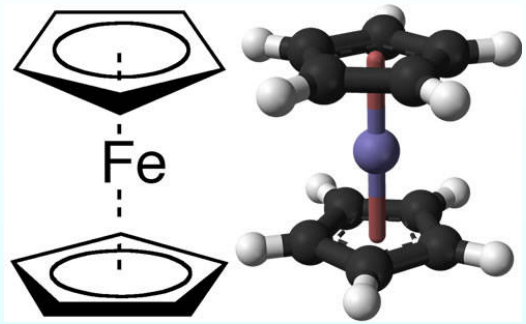


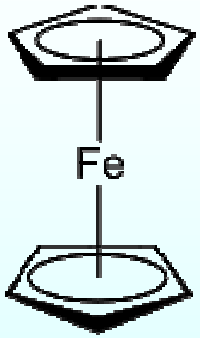
Prospects for "gas-phase" studies

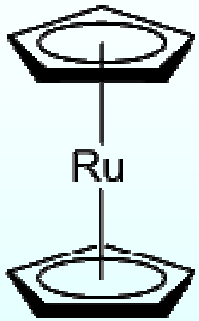
- Gas-phase chromatography:
  - Group 4-8: away from Cl, Br! New types of compounds
    - $M(CO)_6$, M = Mo, W, Sg; $M(CO)_5$, M = Os and Hs
    - organometallics: $M(Cp)_2$, *etc*. M = Os ... Hs
  - Adsorption of atoms on new types of surfaces (SiO_2, sulfure): chemistry on the surface!
  - Adsorption of compounds on metals: 113OH
- Vacuum chromatography:
  - adsorption/desorption of atoms (E115 and E116) on metal surfaces for hot catcher and detection

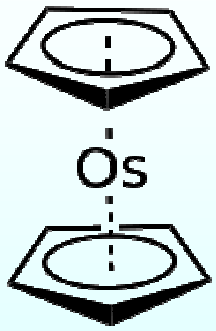
Organometallics

- Metallocene $M(Cp)_2$, M = Fe, Ru, Os and Hs
  - Stable geometry









(3.8 kcal/mol) D_{5d}/D_{5h} D_{5h} D_{5h}

  - Stability: ΔH_{diss} of MCp_2 = M(g) + 2Cp

(kcal/mol):	147	187	187

Carbonyls

- Stability
  - $M(CO)_6 \rightarrow M(CO)_5 + CO$
  - $M(CO)_6 \rightarrow M + 6CO$

Mo < W < Sg

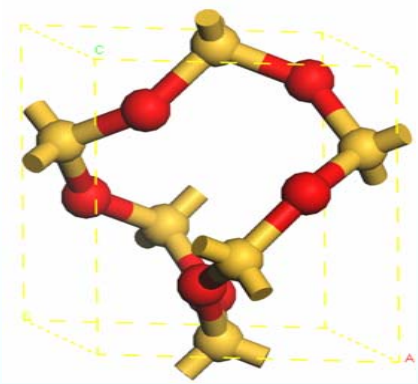
[RECP + CCSD(T): Nash, *et al*.]

- Adsorption on quartz:
  - α, IP, $R_{mol} \sim x$

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

New surfaces: chemistry on the surface

- New surfaces: S, SiO_2
  - optimization of SiO_2 surface at experimental conditions
    - periodic DFT cal-s
  - adsorption of M on SiO_2
    - 4*c*-DFT calculations of M-(SiO_2)



The preferred bulk structure: α quartz at T 25℃ − 180℃ and P_{mm} = 1 atm

[Gao, Anton, Jacob, *et al*.

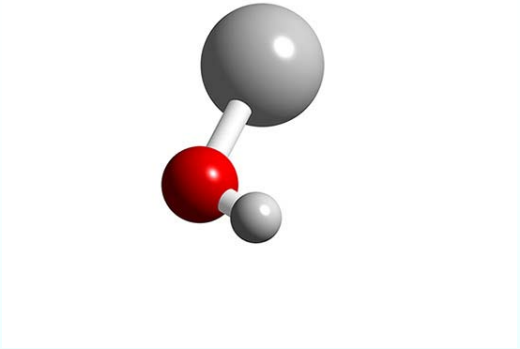
GSI Annual Report 2010]

- Au-Thyols

  $R–(CH_2)n–SH$

  R= OH, F, Cl, Br

Adsorption of volatile compounds: MOH on Au (M = Tl and 113)



M-OH

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

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

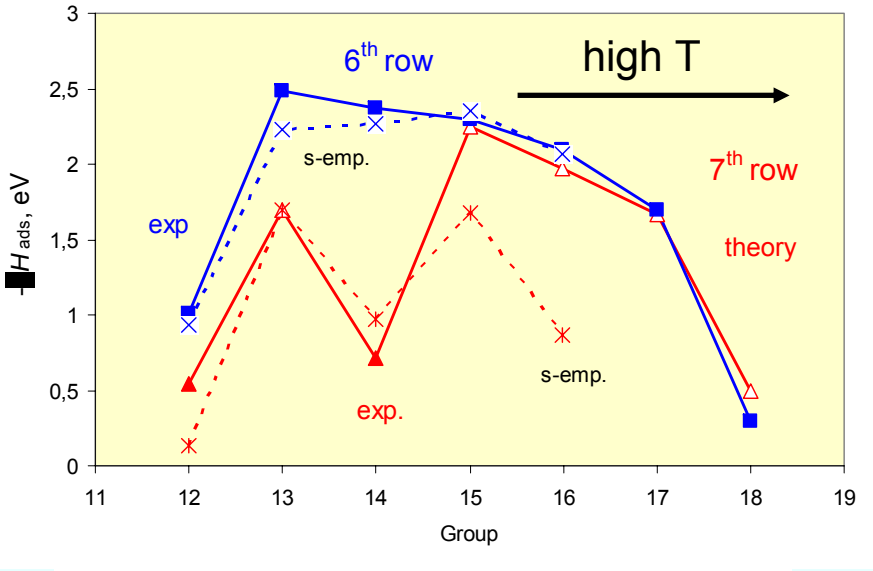
Molecule	R_e, Å	D_e, eV	w_e, cm^{-1}	μ, D	α, a.u.	IP, eV
TlOH	2.19	3.68	547	0.47	45.7	9.262
113OH	2.29	2.42	519	0.45	41.6	9.581

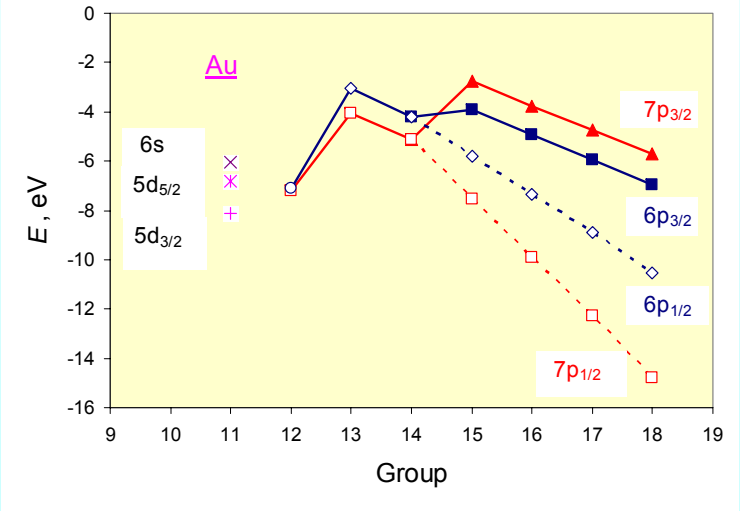
$-\Delta H_{ads}$ of M and MOH on Au

	$-\Delta H_{ads}$, 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)]

Adsorption of Elements Z ≥ 115 on Gold





-ΔH_{ads} on gold, kJ/mol

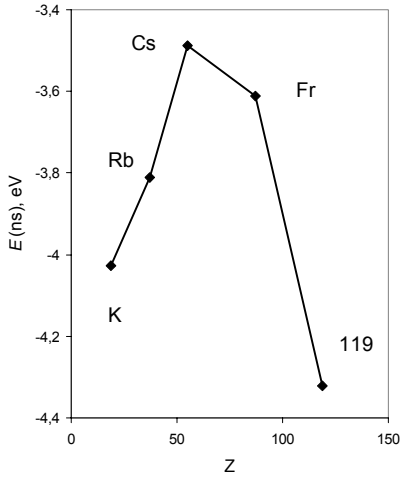
Element	theory	exp.
112	45	52
113	159	-
114	68	35, > 52
115	217	-
116	190	-
117	161	-
118	48	-

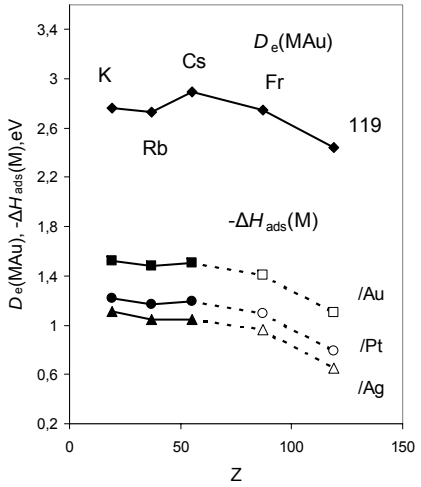
Other noble metals for the hot-catcher?

[V. Pershina, *et al*. JCP 2010]

Adsorption of Elements 119 and 120 on Noble Metals

Group 1:

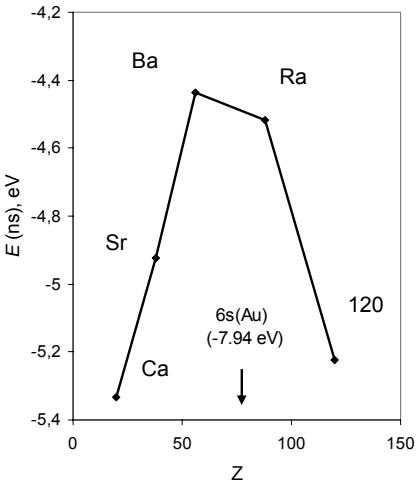


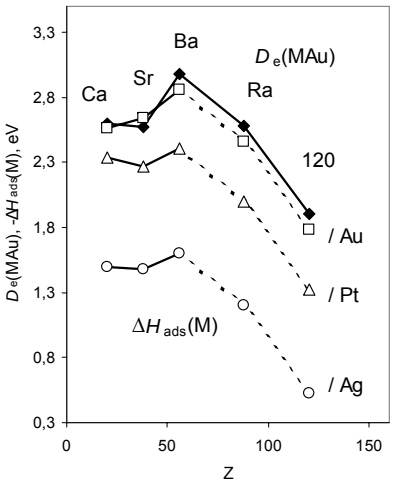


-ΔH_{ads} on noble metals (in kJ/mol)

Surface	E119	E120
Au	106	172
Pt	76	127
Ag	63	50

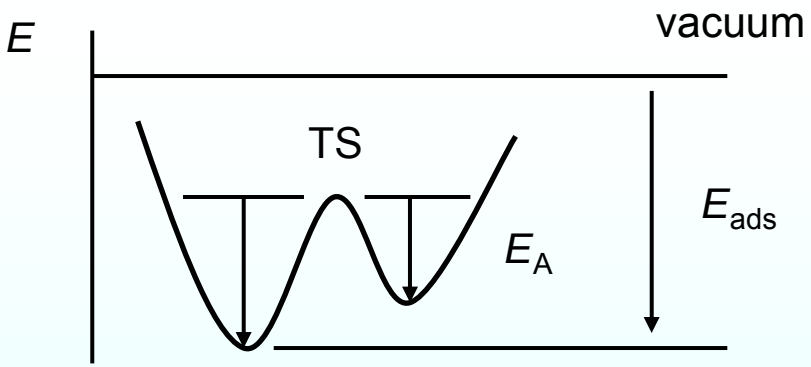
Group 2:



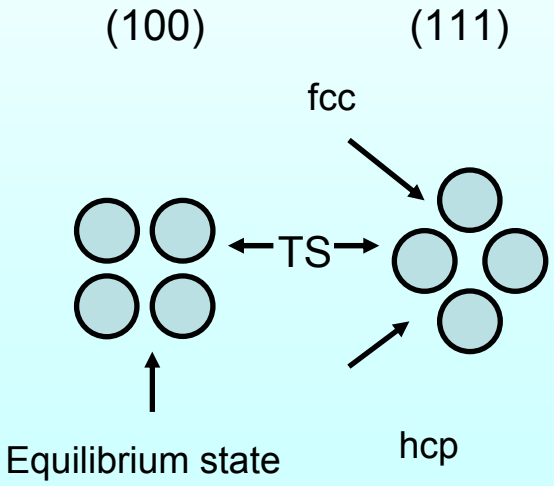


[V. Pershina, *et al*. JCP, 2012]

Predictions of Adsorption/Desorption on Hot-Catcher



Chemisorption on metal surfaces: (DFT) Calculations of adsorption and diffusion



Surface	E_A, eV
Au(100)	0.62
Au(111)	0.22

Complex Formation and Extraction

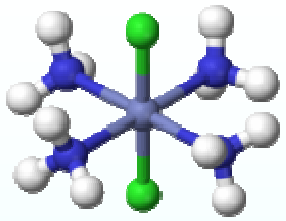
Complex formation:

$$M^{z+} + iL = ML_i^{z-i}$$

$$\beta_i = [ML_i]^{z-i}[M]^{-1}[L]^{-i}$$

$$log\beta_i = -\Delta G^r/2.3RT$$

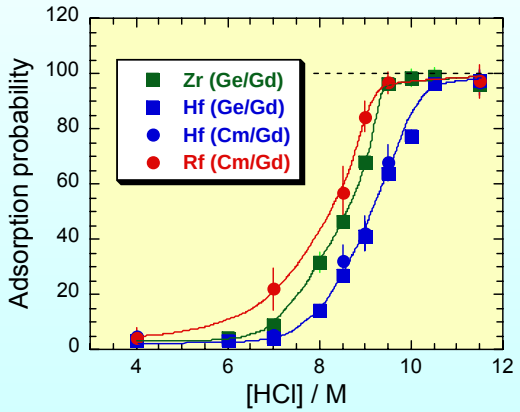
$$\Delta G^r = \Delta G^f(\text{products}) - \Delta G^f(\text{reactants})$$



Anion exchange:

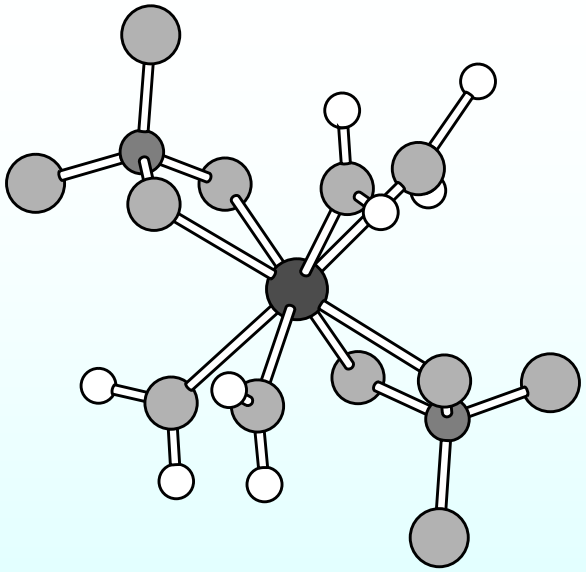
$$pRB^+L^-(org) + ML_i^{-p} \Leftrightarrow (RB^+)_p(ML_i)^{p-}(org) + pL^- \qquad K_{DM}$$

$$K_d = \frac{K_{DM}\left[RB^+L^-\right]^p_{org}\beta_i\left[L^-\right]^{i-p}}{\sum_0^N \beta_n\left[L^-\right]^n}$$



[Y. Nagame, *et al.*]

Complexes of Zr, Hf and Rf in H_2SO_4



$M(SO_4)_2(H_2O)_4$

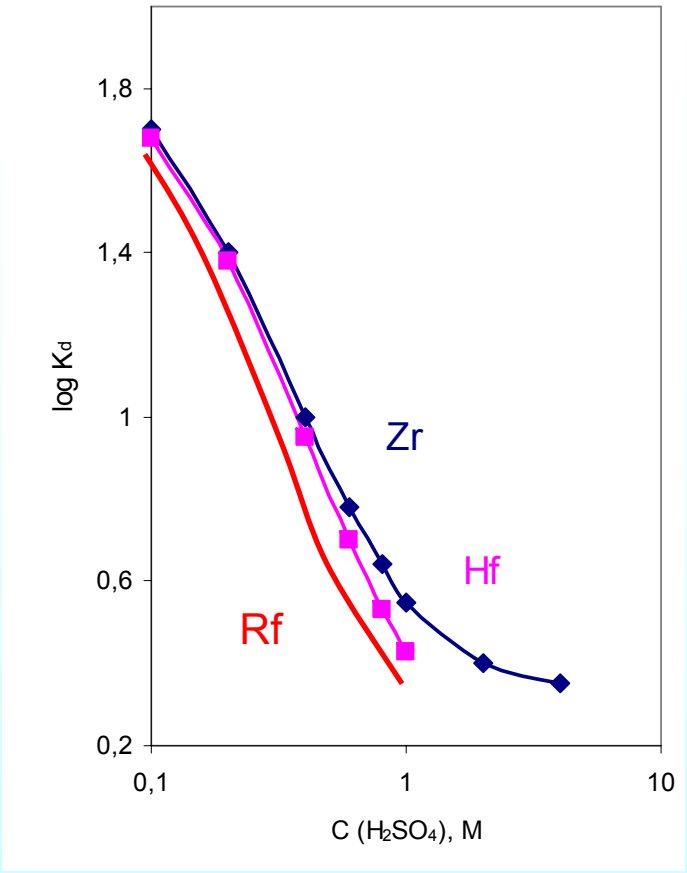
Complex formation reactions:

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

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

Prediction of K_d for Hf and Rf

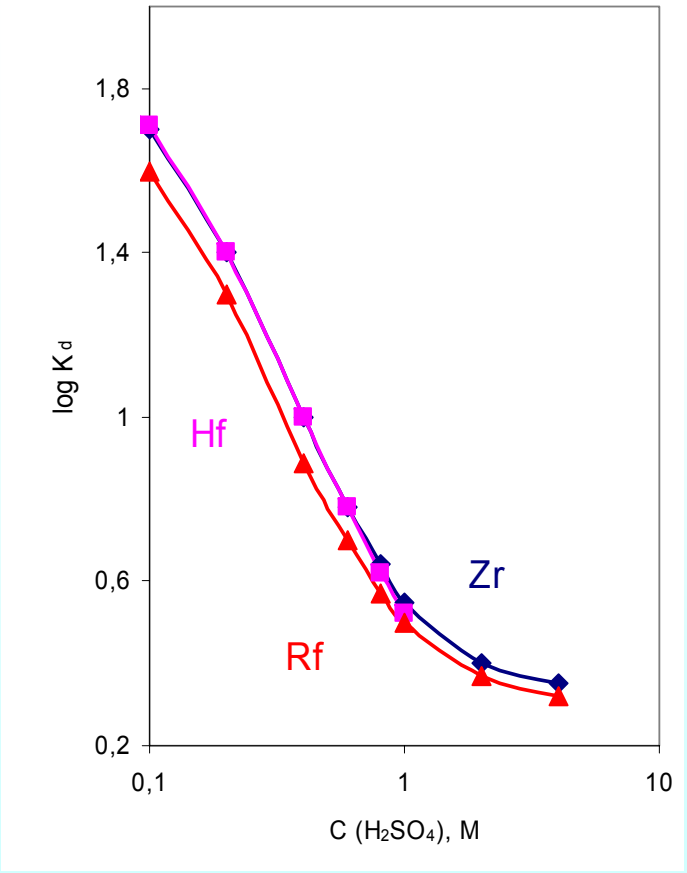
experiment



Zr > Hf > Rf

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

theory



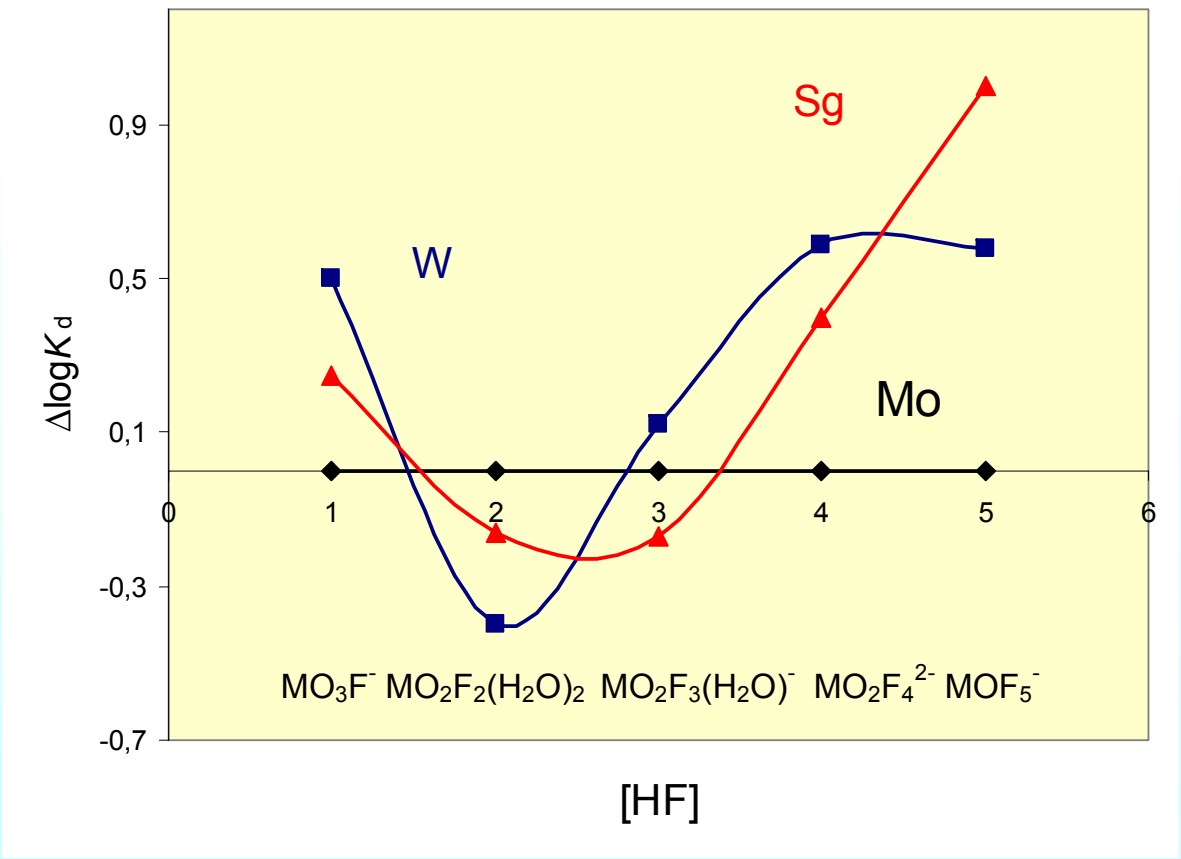
Zr ≥ Hf > Rf

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

Summary of Aqueous Chemistry Studies

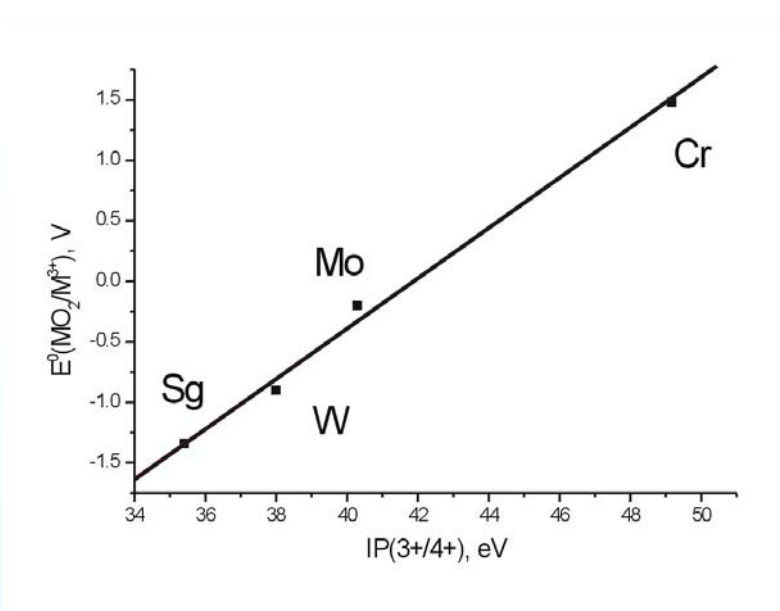
Group	Complexes	Theoretically predicted	Author (Pershina)	Experimentally observed	Author
4	Hydrolysis of M^{4+}	Zr > Hf > Rf	2002	Zr > Hf > Rf	Czerwinski 1992
	$MF_x(H_2O)^{z-x}_{8-x}$ ($x \leq 4$)	Zr > Hf > Rf	2002	Zr > Hf > Rf	Strub 2000, Ishii 2008
	MF_6^{2-}	Rf ≥ Zr > Hf	2002	Rf ≥ Zr > Hf	Trubert 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
6	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

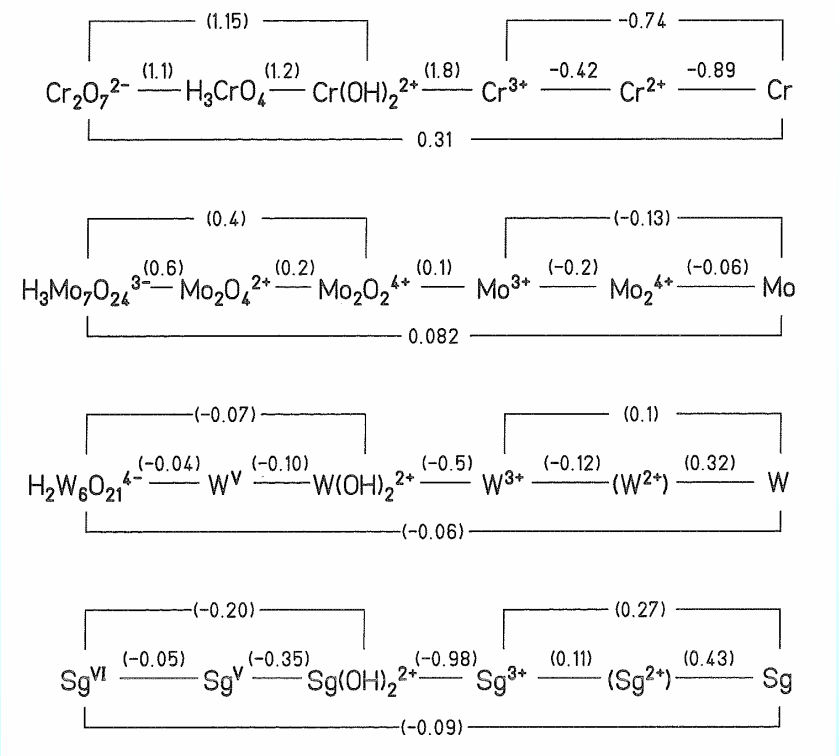
Complex Formation of Sg in HF Solutions



[V. Pershina, RA 2004]

Study of Stabilities of Lower Oxidation States of Sg





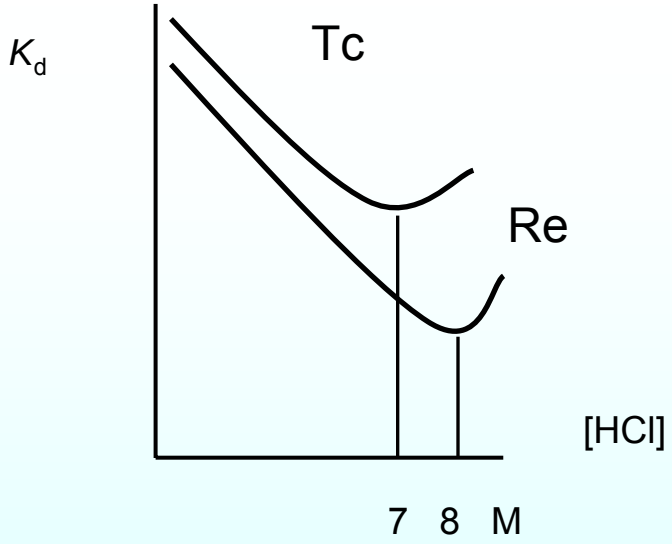
[V. Pershina, RA 1999]

Complex Formation plus Stability of Lower Oxidation States

- $Bh^{VII/IV}$

$MO_4^- + HCl \rightarrow MCl_6^{2-}$

$Tc^{IV} > Re^{IV}$?? Bh^{IV}



- $Hs^{VIII/IV}$

$RuO_4 + nHCl \rightarrow RuCl_5OH^{2-} + Cl_2 + nH_2O$ $\quad E° = 0.14$ V

$OsO_4 + 8HCl \rightarrow H_2OsCl_6 + Cl_2 + 4H_2O$ $\quad E° = -0.36$ V

$Ru^{IV} < Os^{IV}$?? Hs^{IV}

Aqueous Chemistry of Cn and E114

- Stability of $Cn^{II,IV}$
  - Trend: F < Cl < Br < I
  - Complexes: CnI_2, $CnBr_5^-$, CnI_5^-
- Stability of $E114^{II}$
  - Trend: F < Cl < Br < I
  - Complexes: $MX_2 \rightarrow M(OH)X$, $M(OH)_2$, $M(OH)_3^-$
    MBr_3^-, MI_3^-

[V. Pershina, in *The Chemistry of Superheavy Elements*, Ed. M. Schädel, Kluwer, 2003]

New Compounds

- DsF_6
- RgH, RgLi, RgX (X = F, Cl, Br, Au)
- CnF_4 (higher oxidation state of Cn)
- Exotic species:
  - $121X_3$.... $124X_6$
  - $142X_4$, $144F_8$
  - $158O_4$, $160O_4$
  - $164X_2$, $164X_4$

[P. Pyykkö, PCCP 2011]

Summary of Theoretical Studies on the Heaviest Elements

- Methodical
  - usage of relativistic methods is indispensable
  - best developed atomic and molecular codes
  - wave-function and DFT methods are complementary
  - sufficient accuracy for reliable predictions
- Chemical
  - a detailed insight into chemical properties, nature of bonding, interactions
  - reliable predictions of experimental behaviour
  - relativistic effects influence
- Synergy between theory and experiment

Prospects

- Methodical developments
  - Atomic
    - QED effects on the SCF basis
    - Open-shell correlated methods (IHCC, MSCC)
  - Molecular
    - *ab initio* DCB correlated for chemically interesting cases
      - basis sets, correlation techniques
    - *ab initio* predictions of (molecular, adsorption) properties

Prospects: Chemical/Physical Studies

- Systematics of atomic studies
  - α, IP, EA, etc.
- Atomic physics
- New molecular systems
  - metalloriganics, carbonyls
- Adsorption
  - on metal surfaces
  - on other surfaces (S, SiO_2, thyols)
- Fundamental studies (PT, new systems)

Thank you !!!