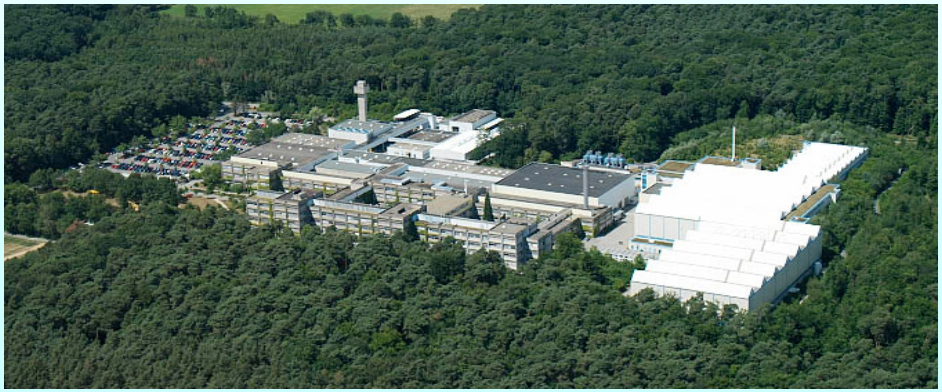
Theoretical Chemistry in Support of Experiment

V. Pershina

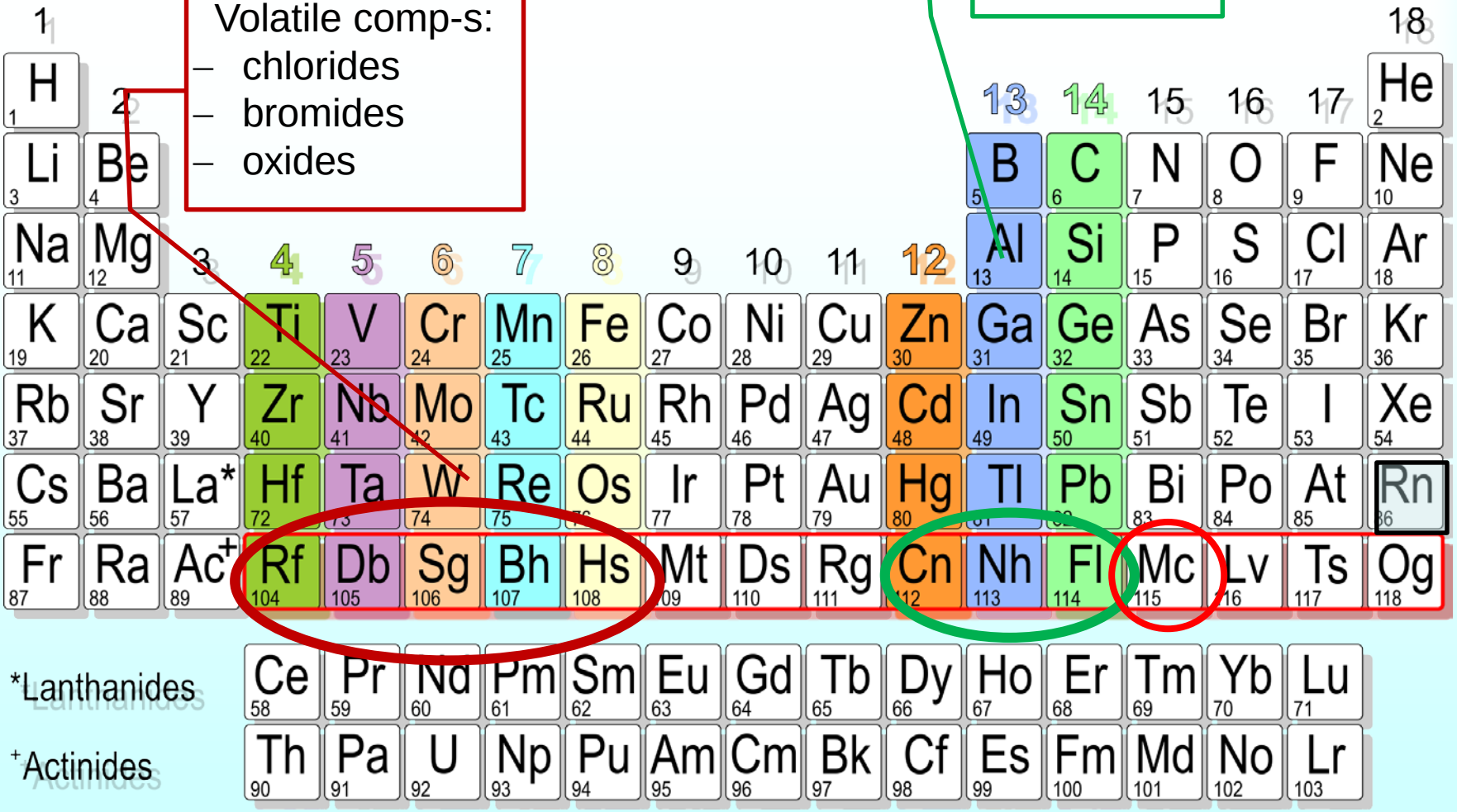
GSI Helmholtzzentrum für Schwerionenforschung, Darmstadt, Germany



Chemical Studies

Volatile comp-s:
- chlorides
- bromides
- oxides

Volatile atoms

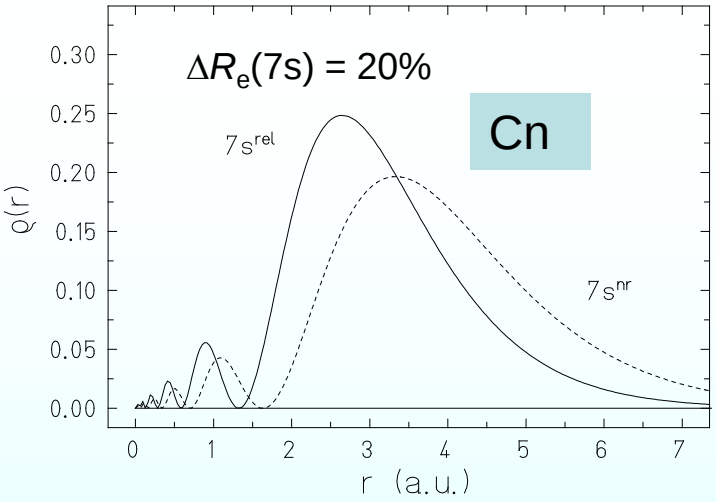


Chemical separation is relatively slow technique – now SHE isotopes with $T_{1/2} < 1$ s can be studied

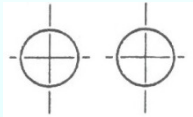
Relativistic Effects on Atomic Orbitals

$$m = m_0 / \sqrt{(1-(v/c)^2}$$

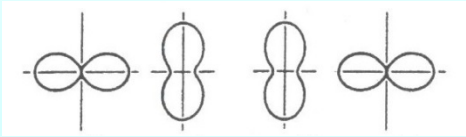
$$a_0 = 4\pi\varepsilon_0\hbar^2 / me^2$$



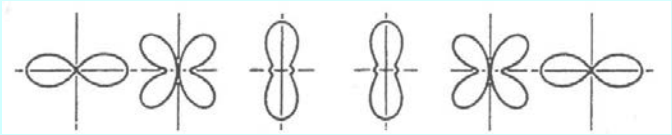
- contraction and stabilization of $s_{1/2}$ and $p_{1/2}$ orbitals



- expansion and destabilization of $p_{3/2}$ and $d_{3/2}$

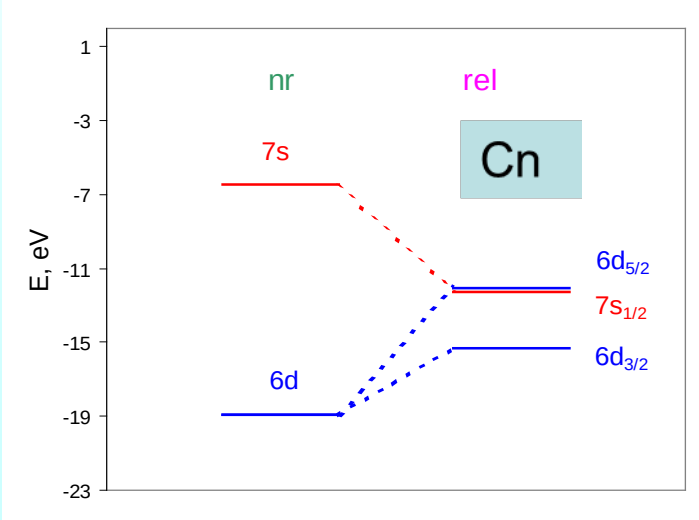


$d_{5/2}$ orbitals

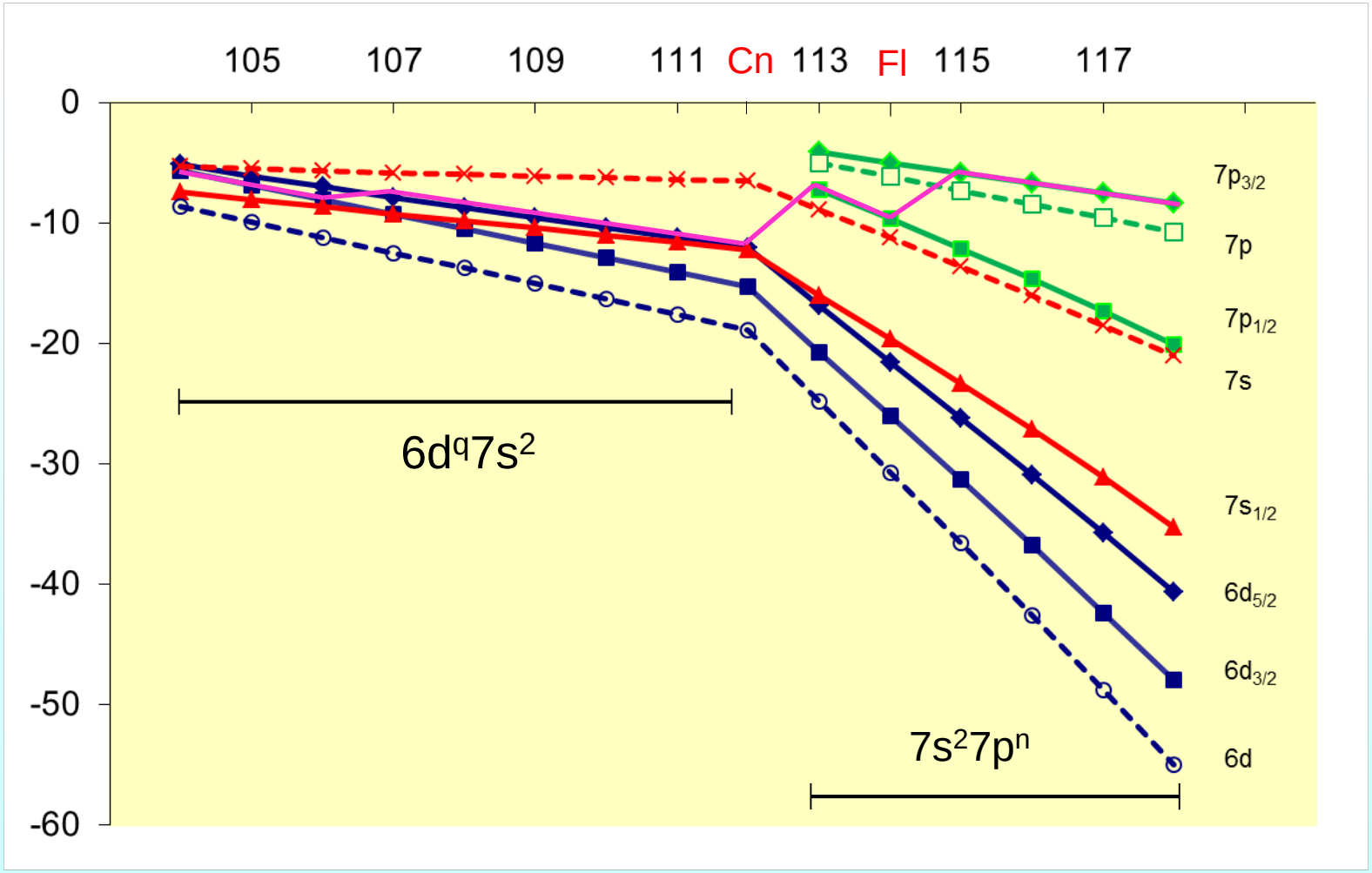


- SO splitting of p, d, f orbitals: $j = l \pm s$

scale as ~ Z^2

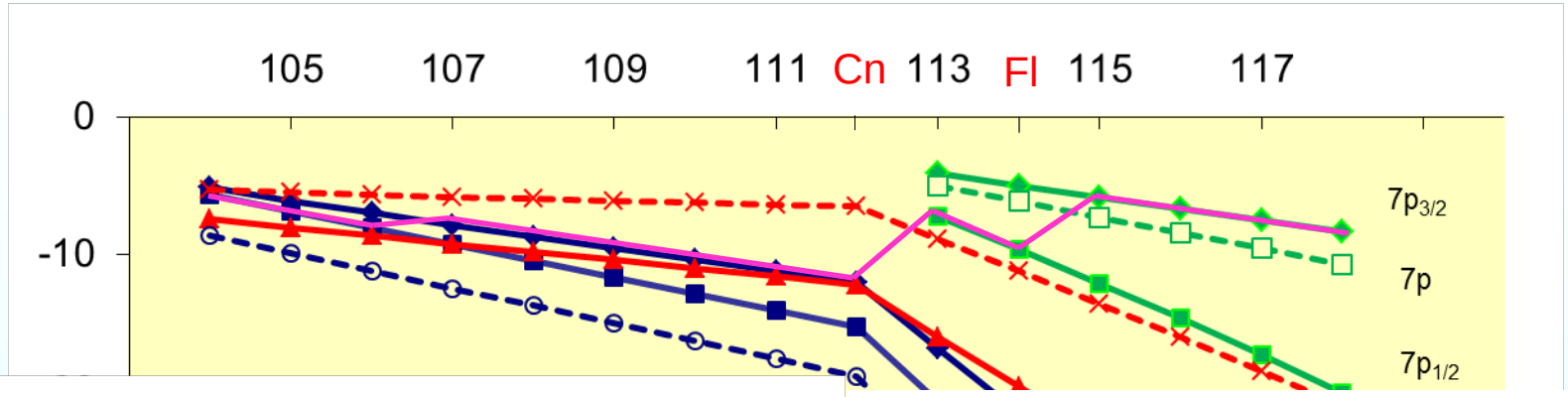


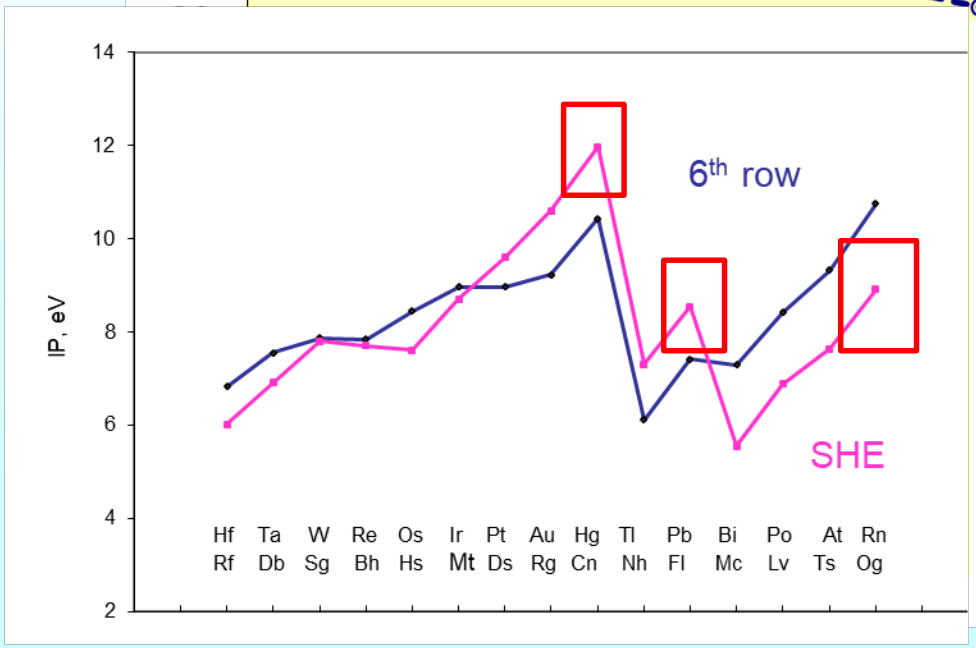
DF and Nonrelativistic Energies of Valence AOs (in eV)

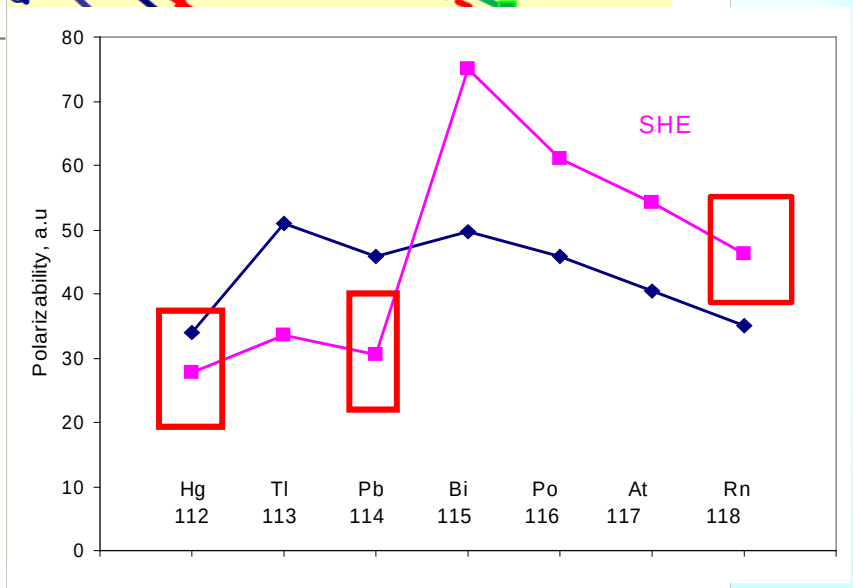


[DF: Desclaux, At. Dat. Nucl. Dat. Tables (1973)]

DF and Nonrelativistic Energies of Valence AOs (in eV)

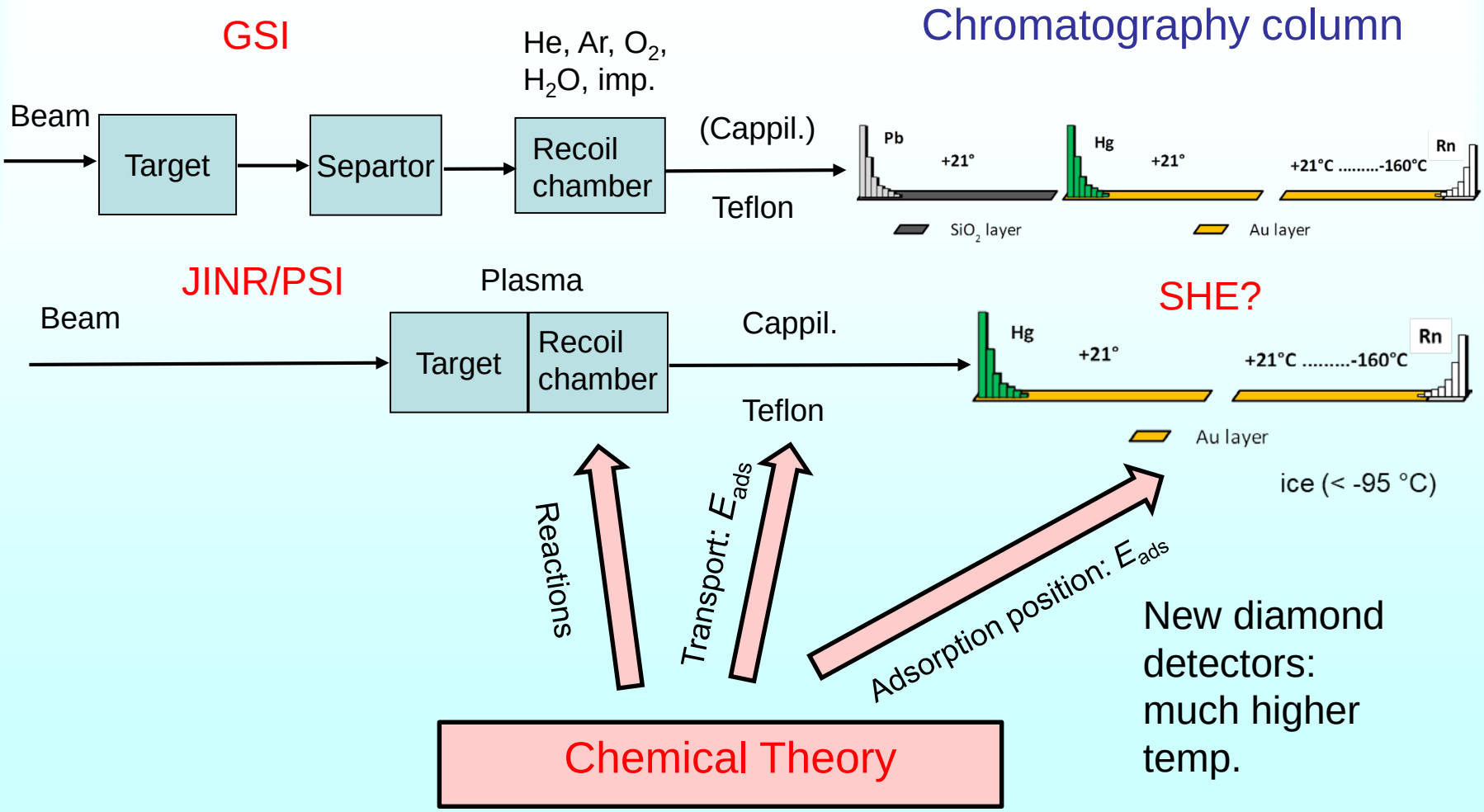






[DF: Desclaux, At. Dat. Nucl. Dat. Tables (1973); DC CC: Eliav, Borschevsky, Pershina, et al.]

Gas-Phase Chromatography Experiments on SHEs



Theoretical Studies of Properties and Volatility of Hg/Cn, Tl/Nh, Pb/Fl and Bi/Mc

- Formation of MO, MO_2 and M(OH) in the atmosphere of O_2, H_2O and H_2
  - reaction energies
  - properties of atoms/molecules (geom., IP, α, μ)
- Predictions of adsorption properties of M, MO, M(OH) on surfaces of quartz and gold
  - structures
  - adsorption energies
  - analysis of bonding

Methods and Softwares – Molecular Codes

- Molecular
  - ADF (SCM)
    - 2c-DFT; SR and SO relativity; all-electron; various E^{xc}; STO basis sets for SHEs
    - energy, properties, fast geometry optimization
    - *commercial & host-locked*
  - DIRAC
    - 2c/4c-DFT + CC – *ab-initio*; all electron, Gaussian orbitals; poor geometry optimization, *free-of-charge*
- Solid state - periodic
  - SCM BAND
    - 2c-SR and SO relativity, all electron, fast geometry optimization, full relaxation, dispersion-corrected Exc , - *commercial & host-locked*

Reaction Energies (in eV) of Gas-Phase Molecules

- Hg

  $Hg + O_2 = HgO + O$ 5.32

  $Hg + O = HgO$ -0.62

- Cn

  $Cn + O_2 = CnOO$ 0.01

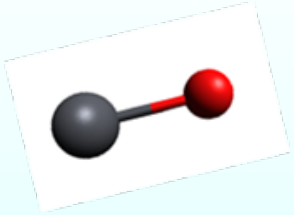
  $Cn + O = CnO$ -0.73

- Fl

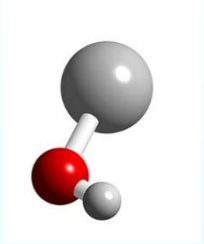
  $Fl + O_2 = FlOO$ -0.04

  $Fl + O = FlO$ -1.95

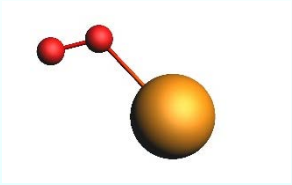
  $Fl + O_2 = OFlO$ -0.003



MO



MOH



MOO

- Rn

  $Rn + O_2 = RnOO$ 0.01

  $Rn + H = RnH$ -0.04

  $Rn + OH = RnOH$ - 0.31

- Og

  $Og + O_2 = OgOO$ -0.003

  $Og + H + OgH$ -0.34

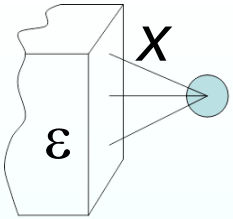
  $Og + OH = OgOH$ -0.83

No reactions with O_2 and H_2O at normal conditions

Calculations of Adsorption Energy

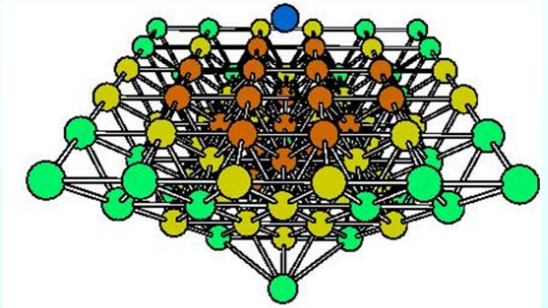
- Adatom-slab model (inert surface)

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



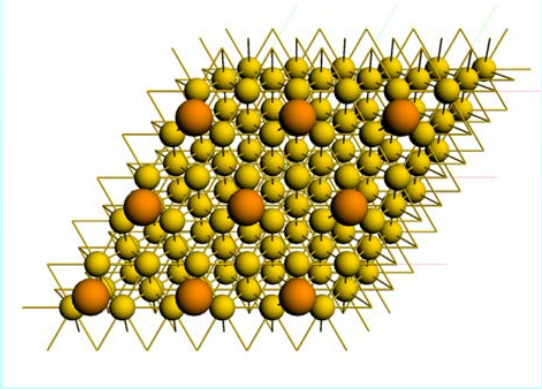
- Cluster model

  (2c/4c-molecular DFT + CC codes, convergence with the cluster size no relaxation, good for atoms)



- Periodic (2c-DFT) calculations

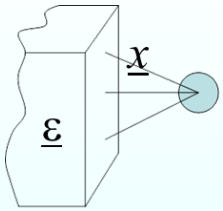
  (slabs, supercells, relaxation, molecules. periodic boundary conditions)

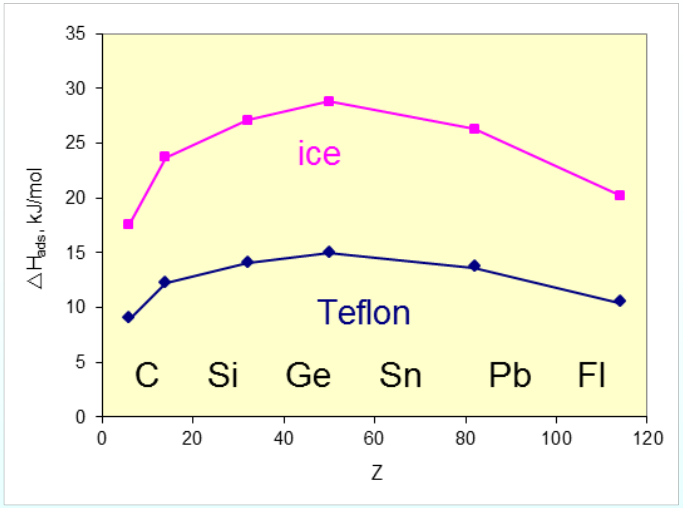


Predictions of SHE Delivery to Chemical Setup

Adatom-slab model:

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





Calculated Properties of Fl ($7s^27p^2$) and 120 ($8s^2$) atoms and ΔH_{ads} on Teflon (DC CCSD(T))

Element	α, a.u.	IP, eV	R_{vdW} Å	ΔH_{ads}, kJ/mol
Fl	29.5	8.539	3.94	10.4
120	162.6	5.851	2.29	35.4

EA(120) = 0.021 eV

$$\frac{N}{N_0} = e^{-\lambda t} = e^{-\frac{\ln 2}{T_{1/2}} t_R}$$

$$t_R = \frac{l a_l}{Q}\frac{u}{4}\tau_0 e^{-\frac{E}{k^B T_C}}$$

E120: $t_{1/2}$=1 s; T_C=25 °C; l = 1m, Q = 1 l/min

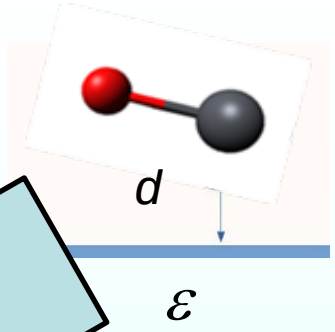
N/N_0= 77 %

[Pershina, et al. JCP 2008, Borschevsky, et al. PRA, 2013]

Calculations of MO Properties and Predictions of ΔH_{ads} on Teflon (DIRAC)

A model for molecule-slab long-range interactions

$$E_{ads}(d) = -\frac{3(\epsilon-1)}{16(\epsilon+2)}\frac{\alpha_{mol}}{\left(\frac{1}{IP_{mol}}+\frac{1}{IP_{surf}}\right)d^3} - \frac{1(\epsilon-1)}{8(\epsilon+2)}\frac{\mu_{mol}^2}{d^3}$$



Calculated R_e [Å]; d_1, and d_2 [Å]; μ_z [D]; IP [...] the upper limits of E_{ads} [kJ/mol] for the two extreme cases rela...

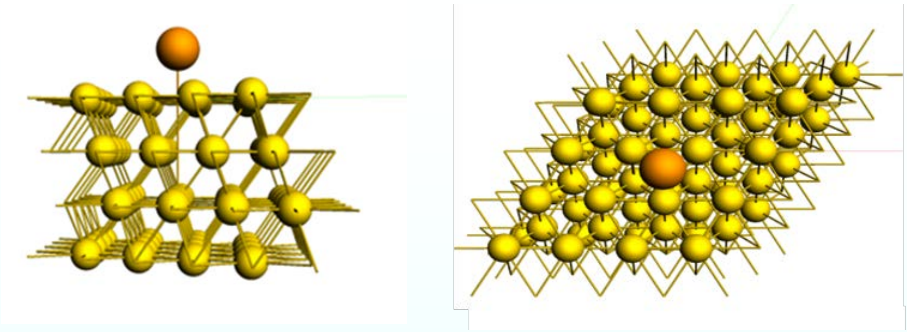
Mol.	R_e(M-O)	d_1	d_2	μ		α_{xx}	α_{zz}	$E_{ads\ (1)}$	$E_{ads\ (2)}$
HgO	1.905	2.270	3.1...		45.31	33.90	68.13	9.94	18.2
CnO	1.887	2		10.38	37.45	30.08	52.19	9.32	10.2
FlO	2.064		,341	4.086	9.76	40.36	31.09	58.90	9.65	13.6

Talk of A. Kotov

A. Kotov, V. Shabaev, et al. *Chem. Phys. Chem.*, submitted

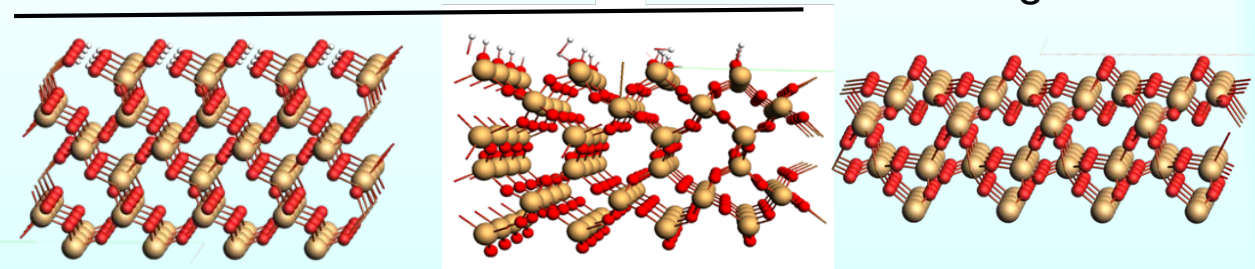
Modeling of Gold and Quartz Surfaces

- Au(111)

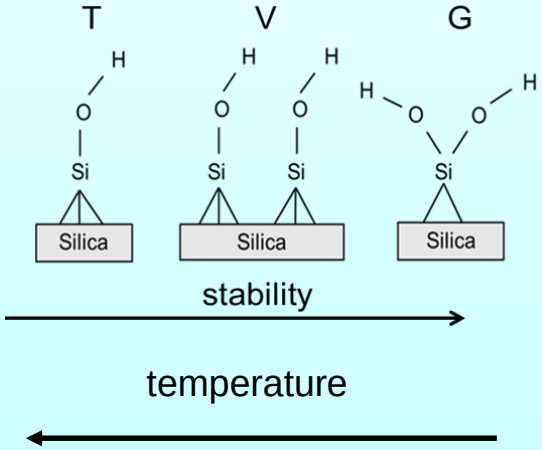


room T → high T

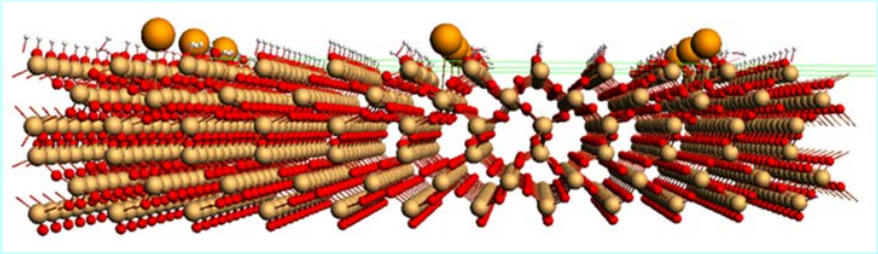
- Quartz



geminal vicinal (80%) bridged

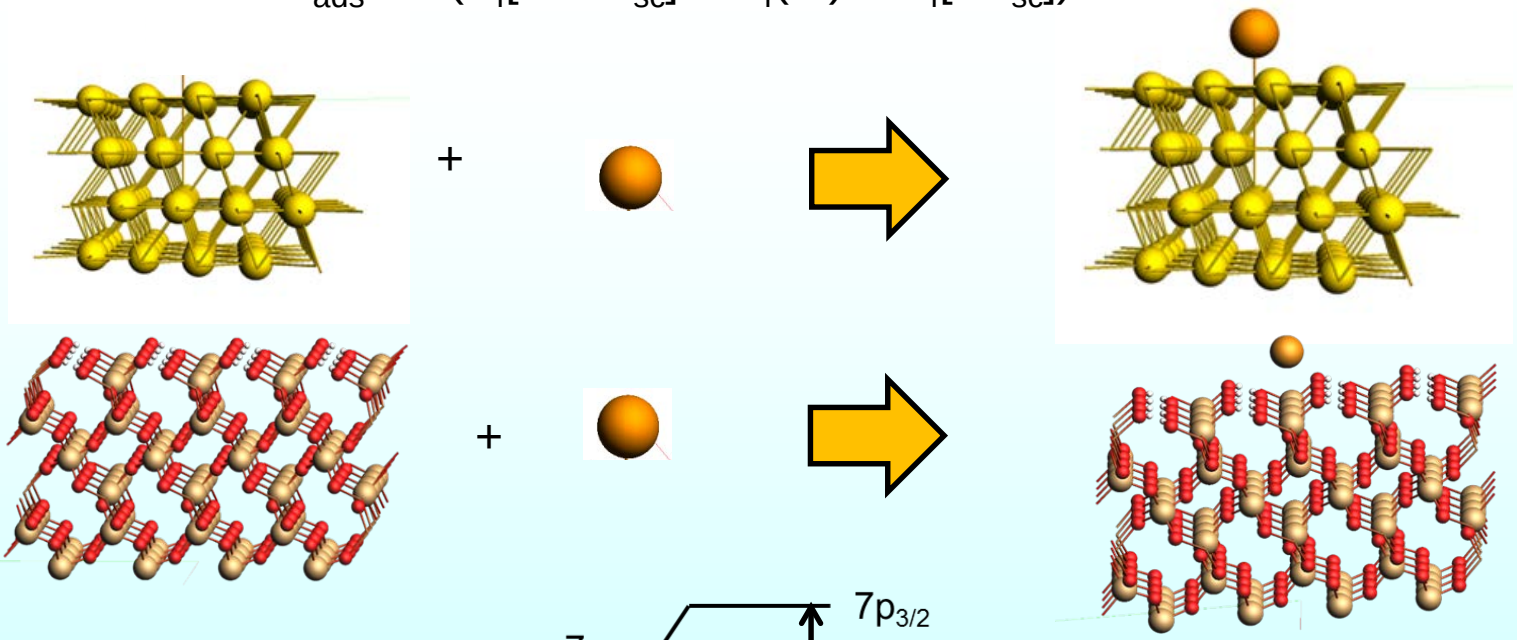


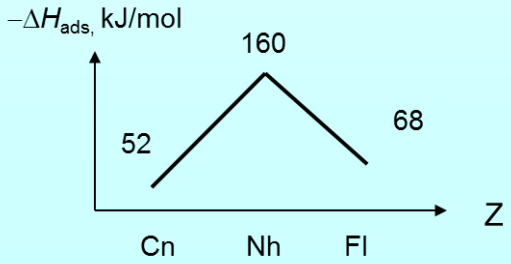
(4 x 4) supercell



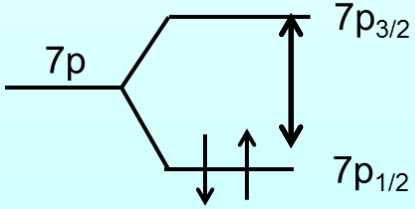
Calculations of E_{ads} of M on Au(111) and Quartz Surfaces

$$E_{ads} = -\left(E_f[\text{M-Au}_{sc}] - E_f(\text{M}) - E_f[\text{Au}_{sc}]\right)$$





Fl

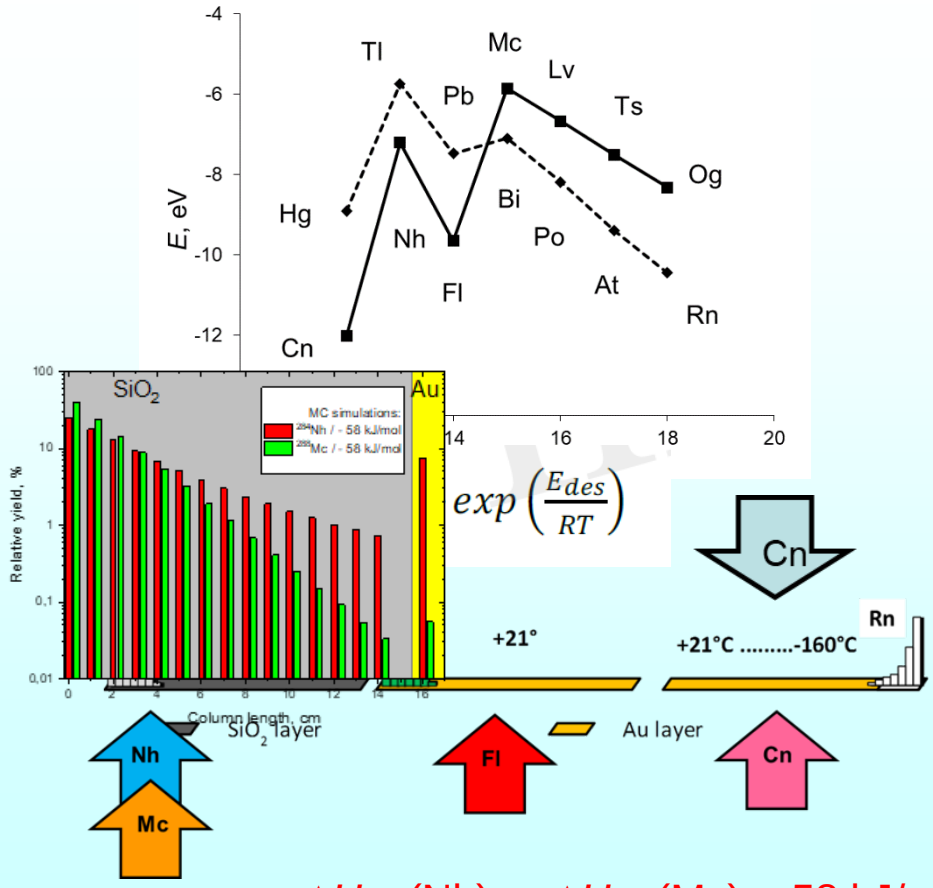


SO

E_f(SO): Cn: 0 eV
Nh: 2.01 eV (194 kJ/mol)
Fl: 5.12 eV (494 kJ/mol)

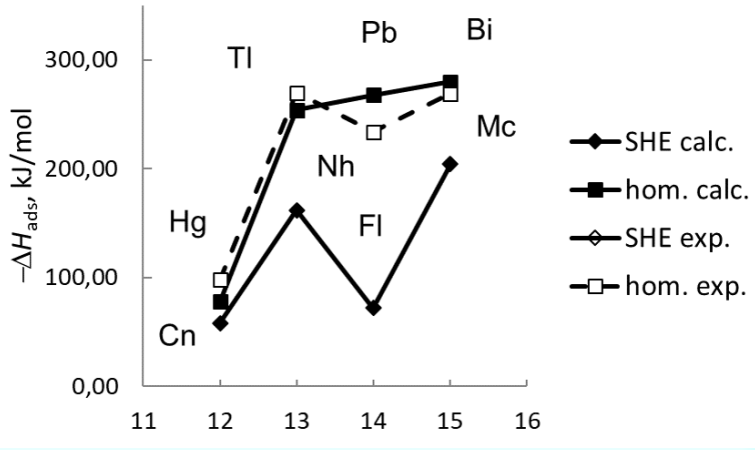
Calculations of E_{ads} of Group 12-15 Elements on Gold and Quartz

AOs



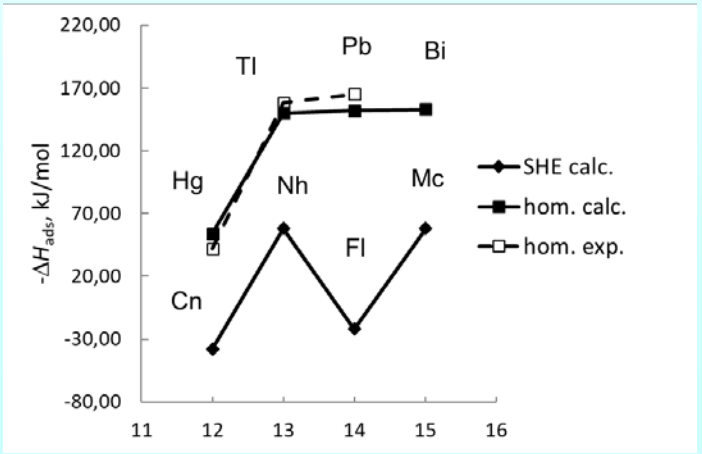
$-\Delta H_{ads}(Nh) = -\Delta H_{ads}(Mc) = 58$ kJ/mol

M/Gold



(revPBE-D3BJ)

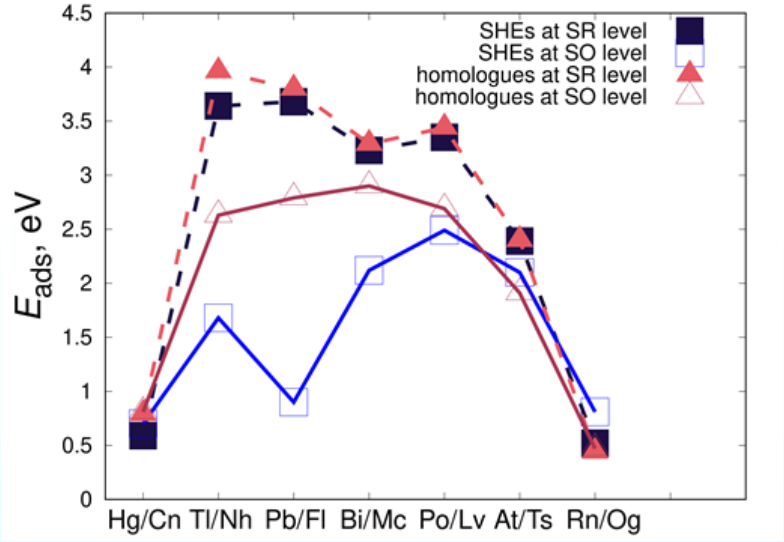
M/Quartz

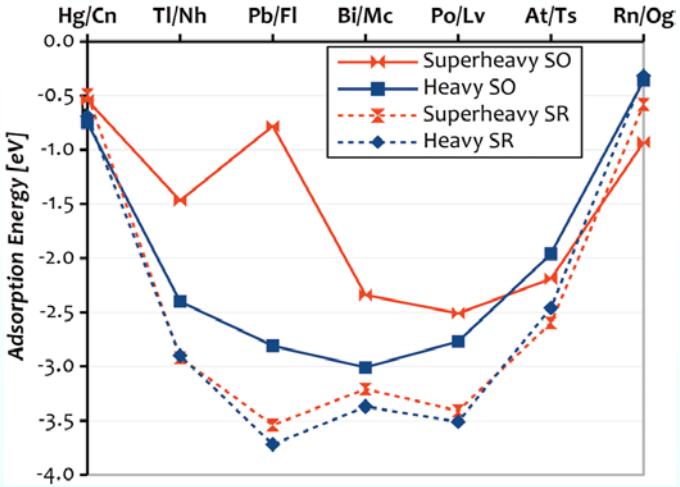


V. Pershina. M. Ilias, A. Yakushev, *Inorg. Chem*. **60**, 9796 (2021)

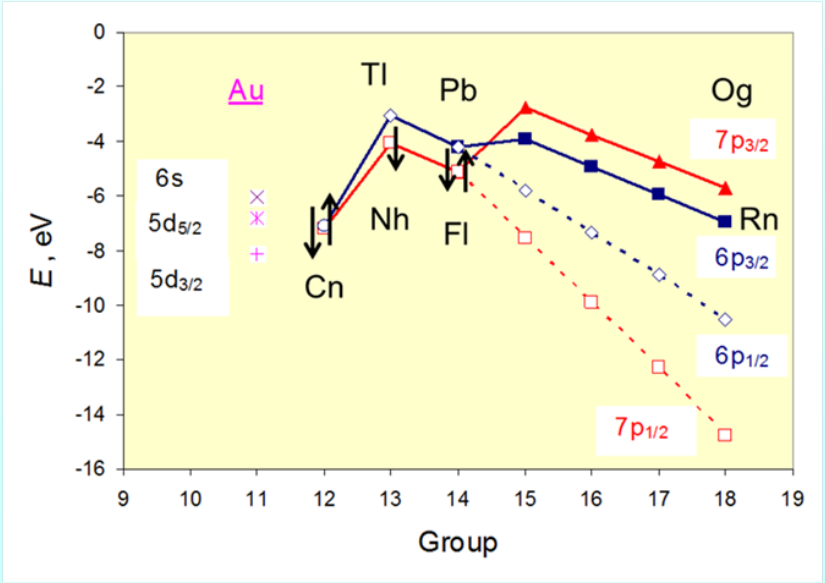
A. Yakushev: experiment on Nh and Mc, to be published

Adsorption of SHEs on the Au(111) Surface





[L. Trombach et al., PCCP 21,18048 (2019)]



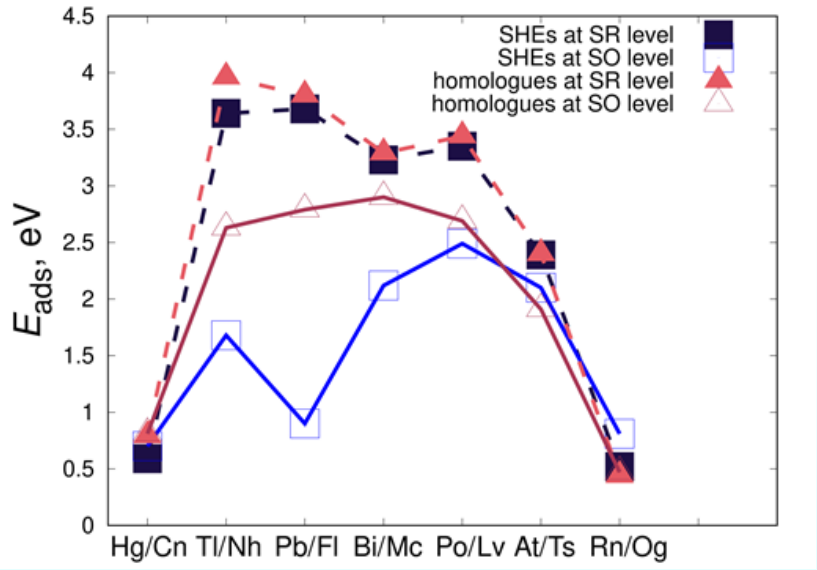
-ΔH_{ads} on gold, kJ/mol

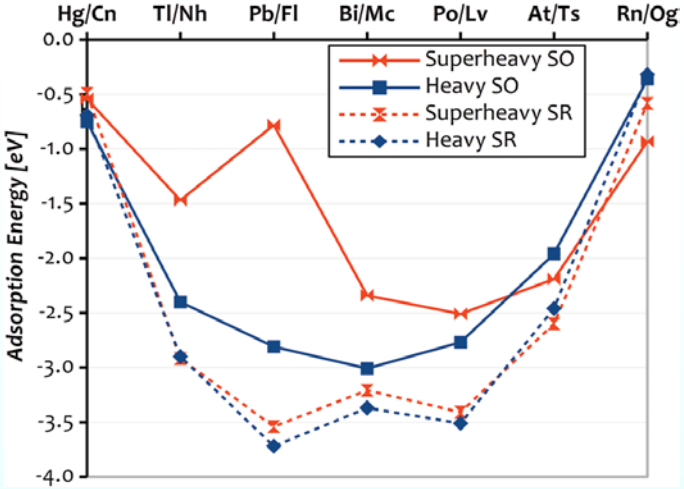
Element	theory	exp.
Cn	45	52
Nh	159	-
Fl	68	35, > 52
Mc	217	-
Lv	190	-
Ts	161	-
Og	78	-
	70 (Tr)	

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

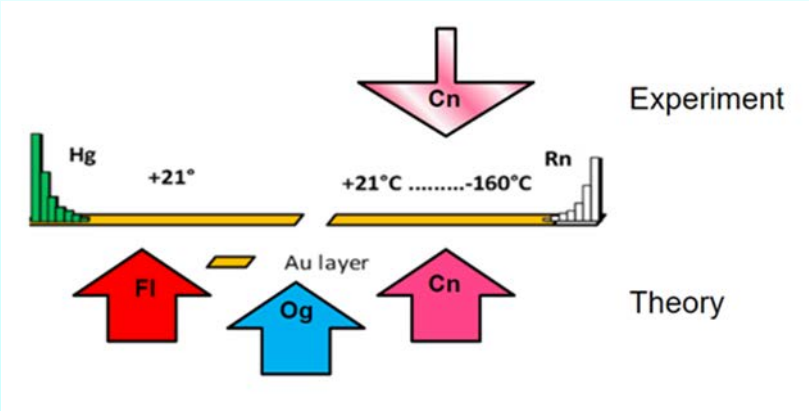
[A. Rhyzhkov, V. Pershina, *et al*., PCCP, 2023]

Adsorption of SHEs on the Au(111) Surface





[L. Trombach et al., PCCP 21,18048 (2019)]



Only Cn, Og and Fl can me measured

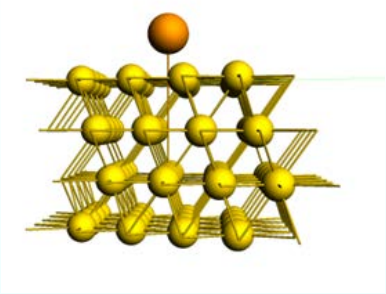
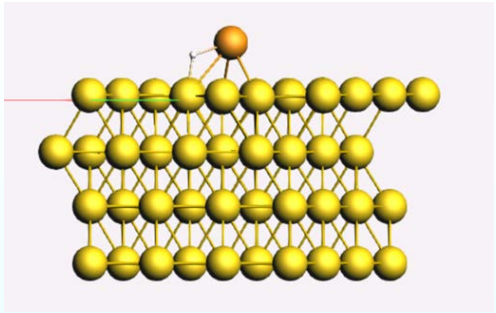
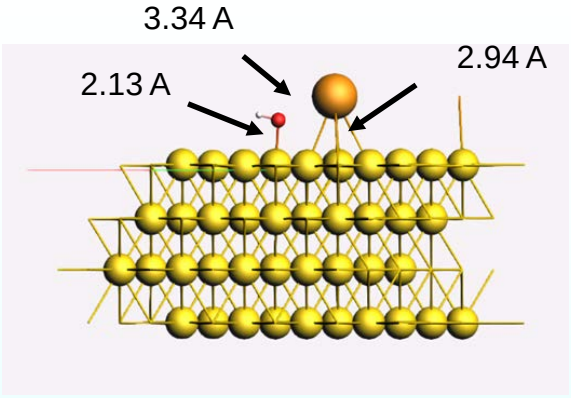
-ΔH_{ads} on gold, kJ/mol

Element	theory	exp.
Cn	45	52
Nh	159	-
Fl	68	35, > 52
Mc	217	-
Lv	190	-
Ts	161	-
Og	78	-
	70 (Tr)	

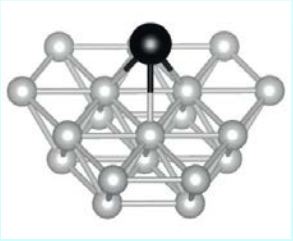
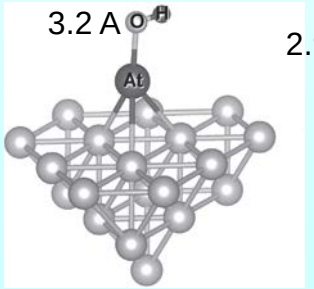
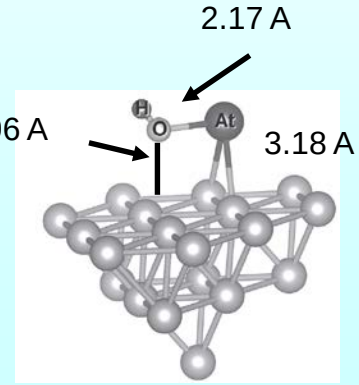
[V. Pershina, *et al*. JCP 2010]

[A. Rhyzkov, V. Pershina, *et al.* PCCP, 2023]

Adsorption of At, AtH and AtOH on the Au(111) Surface: Comparison of Periodic *vs* Cluster Approach

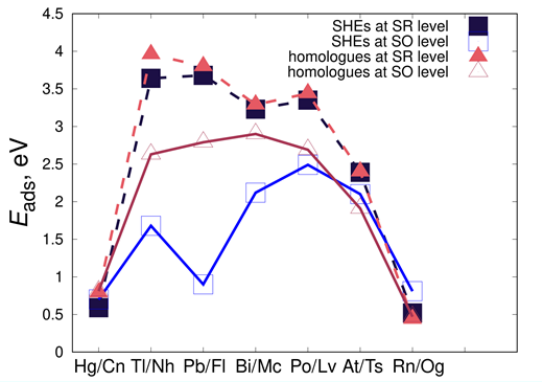
	At	AtH	At-OH (2.15 A)
BAND			
E_{ads}(kJ/mol)	184	164	185

Cluster: small size, no relaxation, no dispersion

	[Y. Demidov, *et al*., CPL, **691**,126 (2018)]		
E_{ads}(kJ/mol) 130 ± 10	-	80-100	30-50

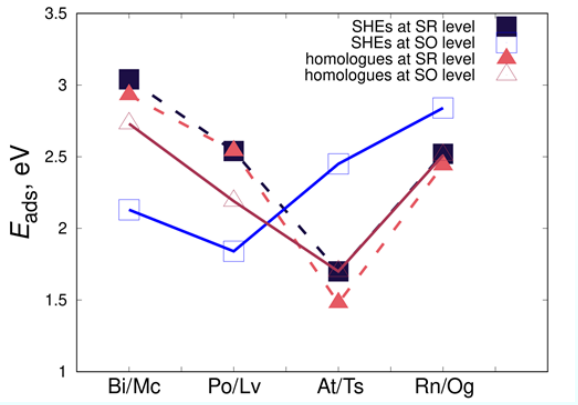
E_{ads} (in kJ/mol) of M, MH and MOH on the Au(111) Surface

M



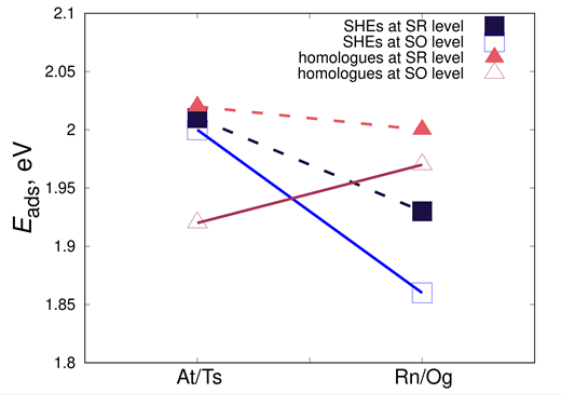
	6th row		7th row
Atom	SO	Atom	SO
Bi	280	Mc	204
Po	259	Lv	240
At	184	Ts	203
Rn	45	Og	78

MH



	6th row		7th row
Molecule	SO	Molecule	SO
BiH	263	McH	205
PoH	211	LvH	177
AtH	164	TsH	239
RnH	242	OgH	274

MOH



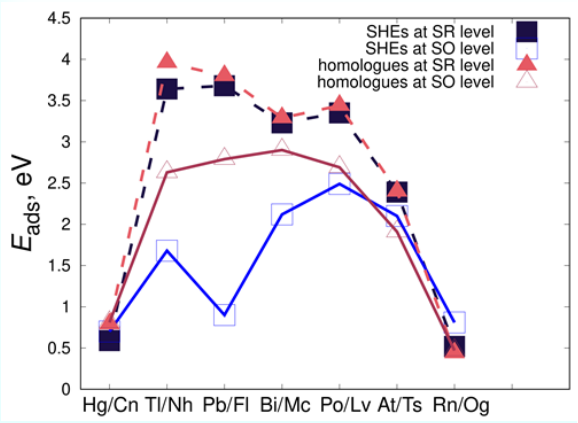
	6th row		7th row
Molecule	SO	Molecule	SO
AtOH	185	TsOH	193
RnOH	190	OgOH	179

Trend reversal

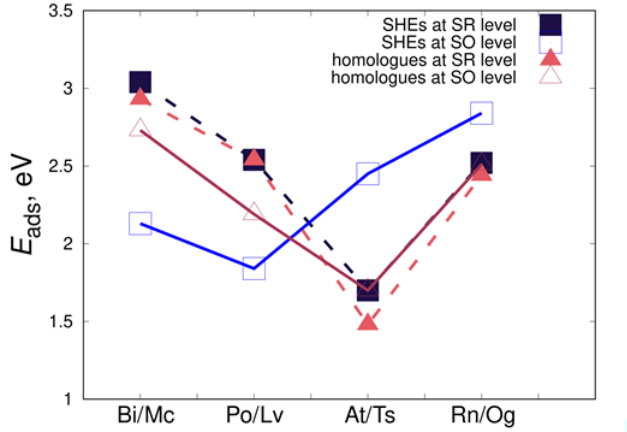
Gr 15:	Bi > Mc	BiH > McH	
Gr 16:	Po > Lv	PoH > LvH	
Gr 17:	At < Ts	AtH < TsH	AtOH < TsOH
Gr 18:	Rn < Og	RnH < OgH	RnOH > OgOH

E_{ads} (in kJ/mol) of M, MH and MOH on Gold

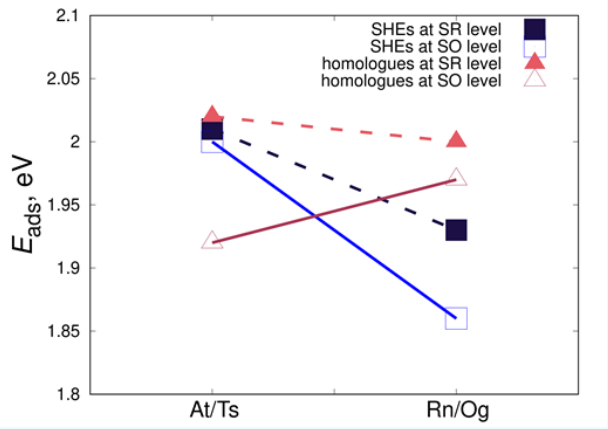
M



MH



MOH

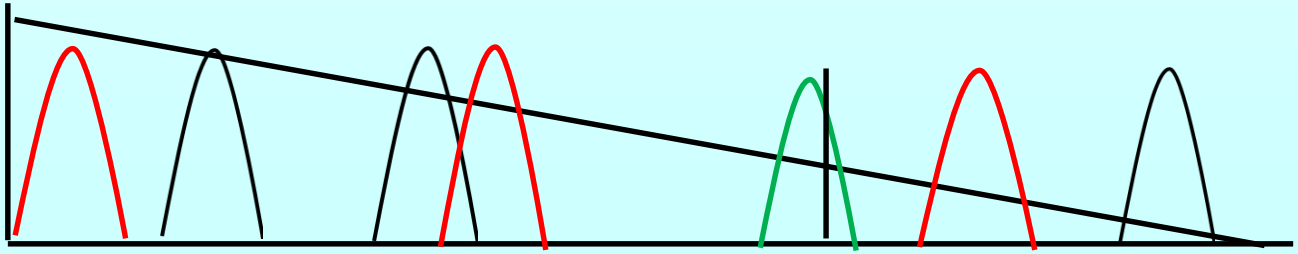


RnH < OgH RnOH > OgOH Rn < Og

D_e (in eV) 0.03 < 0.27 0.31 < 0.83

242 < 274 190 > 180 45 < 78

1000 C



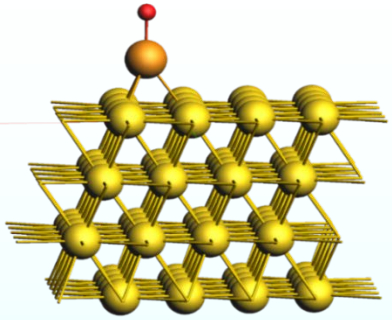
A. Rhyzhkov, V. Pershina, M. Ilias, V Shabaev, PCCP, 2023

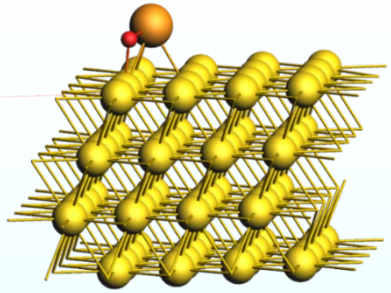
E_{ads}(M/MO) (in eV) on Au(111) Surface

HgO/CnO

PbO/FlO

s^2d^{10}



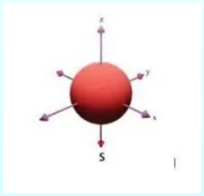


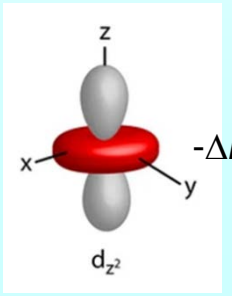
s^2p^2

Property	Approx.	HgO	CnO	PbO	FlO
E_{ads}(MO)	SR	2.28	1.92	1.92	2.22
	SO	2.29	1.93	1.88	1.88

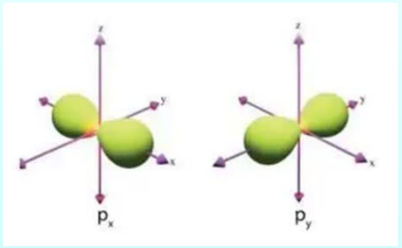
Property	Approx.	Hg	Cn	Pb	Fl
E_{ads}(M)	SR	0.79	0.60	3.80	3.76
	SO	0.81	0.62	2.79	0.92

AOs

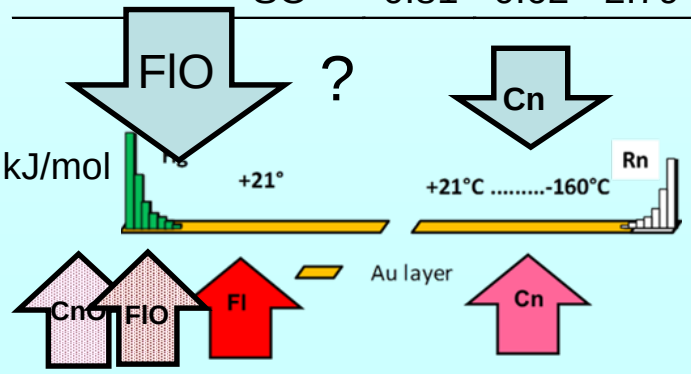




AOs



$-\Delta H_{ads} < 60$ kJ/mol



Experiment

Theory

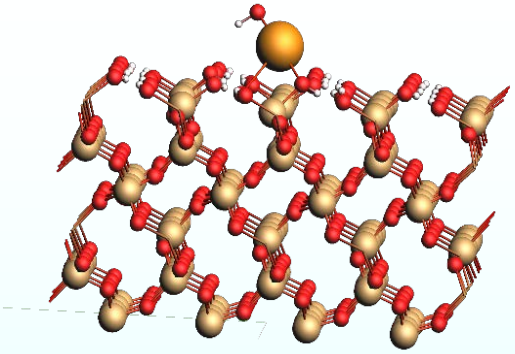
[V. Pershina and M. Ilias, *Dalton Trans.* **51**, 7321 (2022)]

E_{ads}(M/MO) on Quartz (Geminals) (in eV)

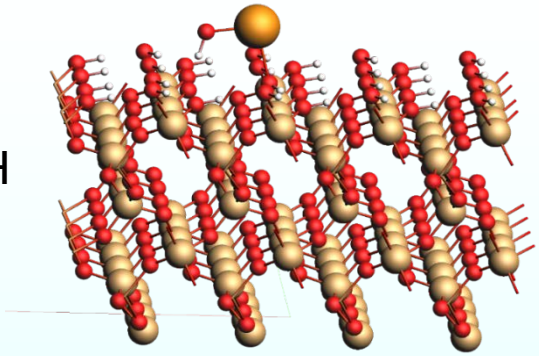
HgO/CnO

PbO/FlO

s^2d^{10}



OH-SiO_2-MOH

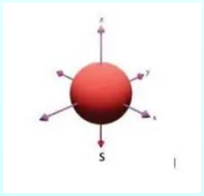


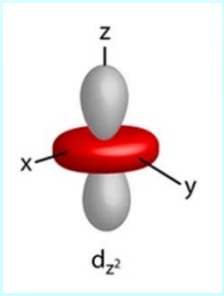
s^2p^2

Property	Approx.	HgO	CnO	PbO	FlO
E_{ads}(MO)	SR	2.27	1.39	1.22	2.80
	SO	2.18	1.01	1.06	1.64

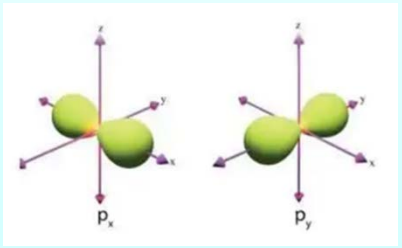
Property	Approx.	Hg	Cn	Pb	Fl
E_{ads}(M)	SR	0.28	0.29	0.72	0.15
	SO	0.28	0.29	0.22	-0.22

AOs



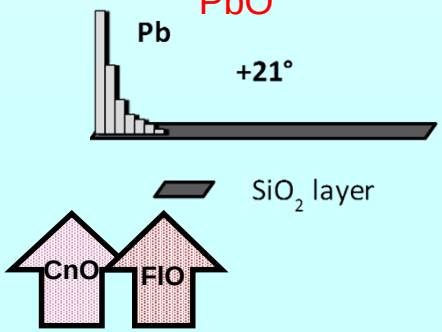


AOs



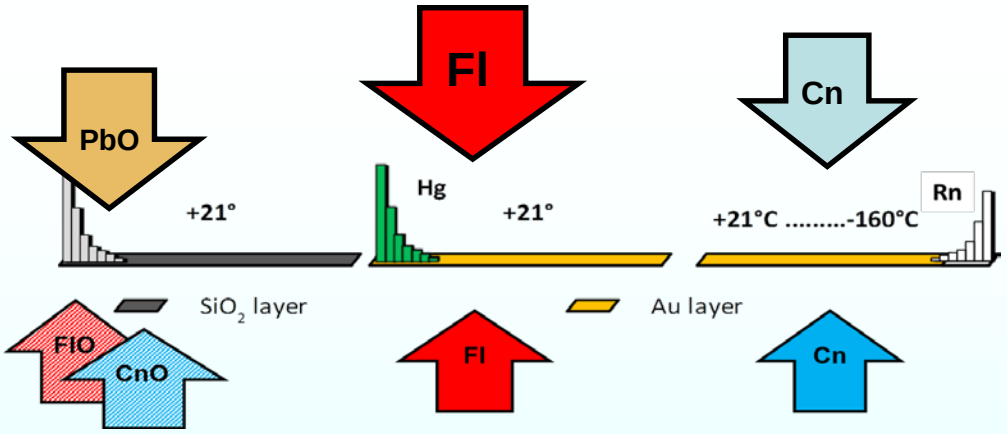
165 kJ/mol
> 67 kJ/mol

PbO



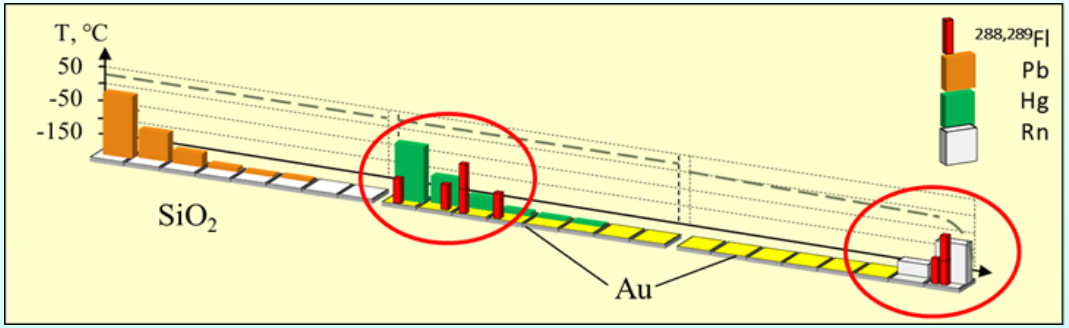
Theory: desorption as PbO
Pb on reactive surface
PbO on stable surface

E_{ads}(M/MO) on Quartz and Gold



experiment

theory



Theory: V. Pershina and M. Ilias, *Dalton Trans.* **51**, 7321 (2022)

Experiment: A. Yakushev, *et al*. *Frontiers in Chemistry* (2022)

Element 118, Og, is Solid?

Adsorption of inert gases including element 118 on noble metal and inert surfaces from *ab initio* Dirac–Coulomb atomic calculations

V. Pershina,[1,a)] A. Borschevsky,[2] E. Eliav,[2] and U. Kaldor[2]
[1]*Gesellschaft für Schwerionenforschung, D-64291 Darmstadt, Germany*
[2]*School of Chemistry, Tel Aviv University, 69978 Tel Aviv, Israel*

J. Chem. Phys. **129**, 144106 (2008)

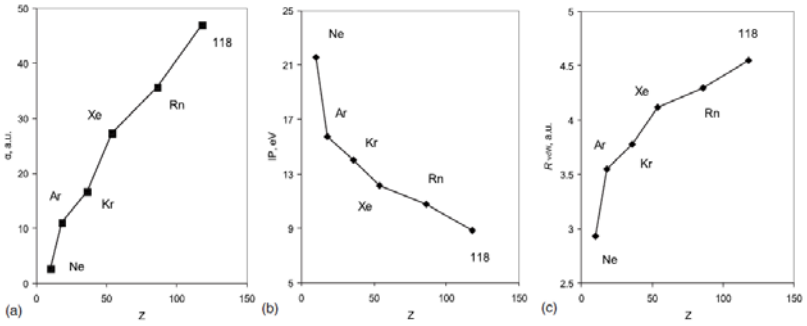
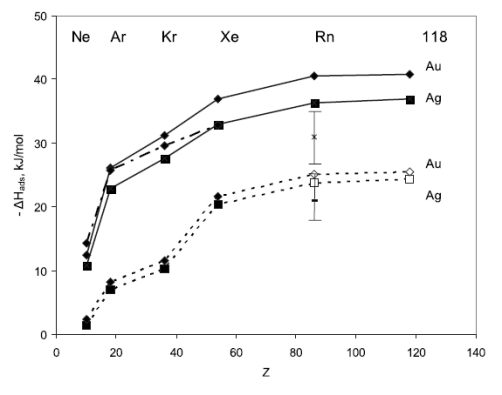


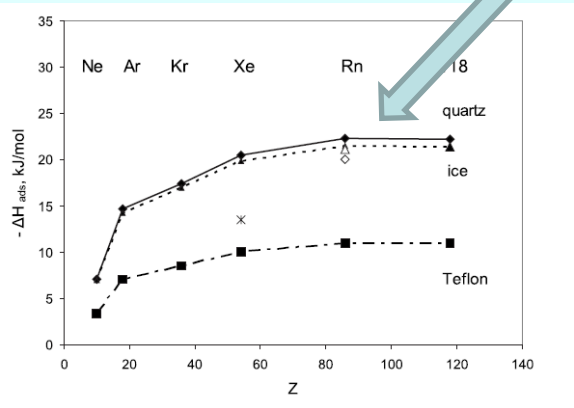
FIG. 1. [(a)–(c)] Properties of rare gas atoms: (a) Polarizabilities α; (b) IPs; (c) vdW radii R_{vdW} (see Table III). The experimental α and IP values of Ne hrough Xe are those of Ref. 16. R_{vdW} from Refs. 11, 13, and 21. The values for element 118 and α(Rn) are from present calculations.

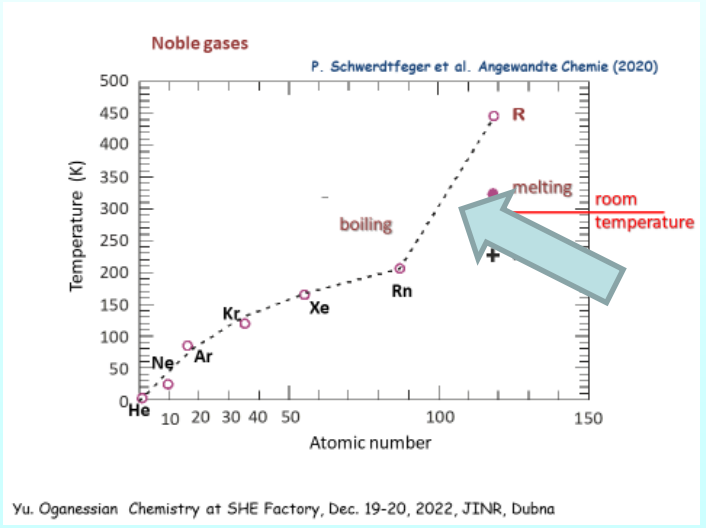
Van der Waals interaction energy

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

Physisorption on various surfaces







Drastic increase from Rn to Og. Why so??

Acknowledgements

- M. Iliaš, University Banska Bystrica, Slovakia
- A. Rhyzhkov, St. Petersburg University
- Dubna JINR computing center

Thank you!