Relativistic Effects on Properties of the Elements at the End of the Periodic Table

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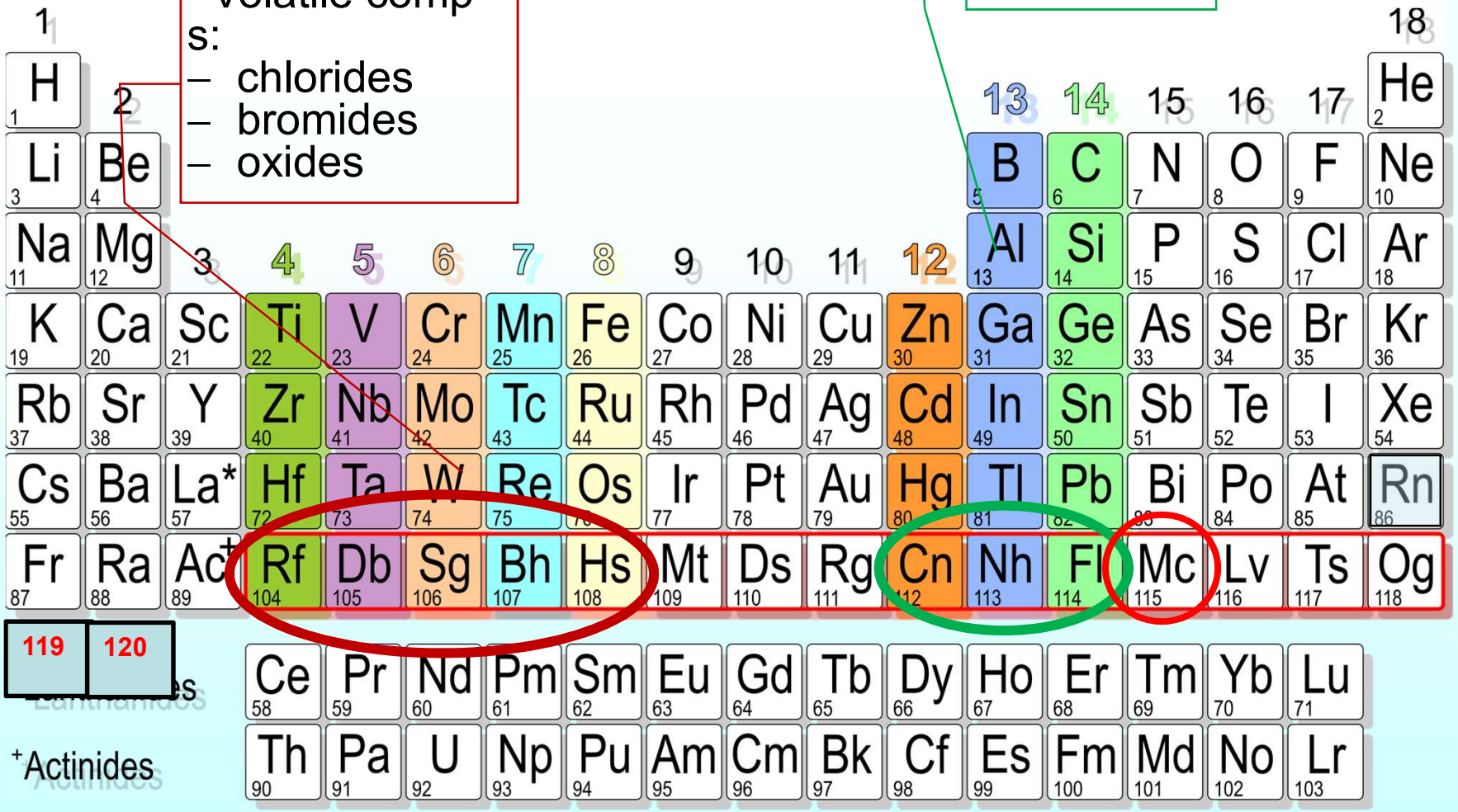
Chemical Studies

Volatile comp-s:
- chlorides
- bromides
- oxides

Volatile atoms



Chemical separation is relatively slow technique – $t_{1/2} < 1$ s can be studied

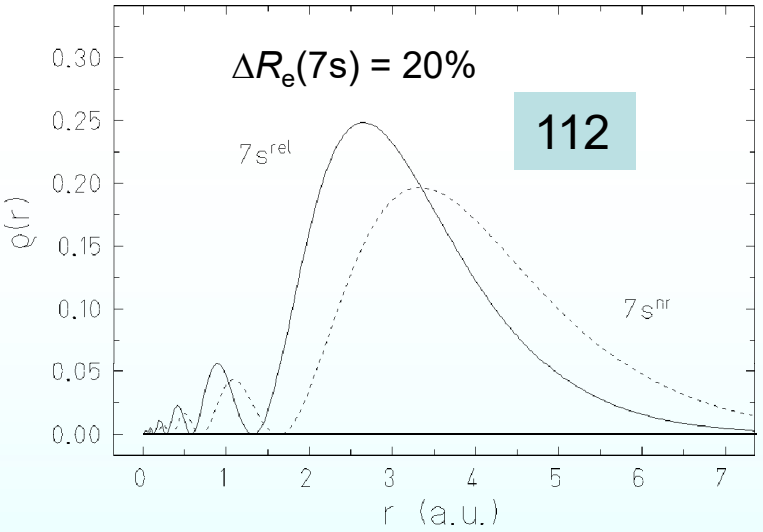
$^{50}Ti + {}^{249}Cf \rightarrow {}^{295}120$ and $^{296}120$ $\quad t_{1/2} = 7 - 40$ μs

Relativistic Effects

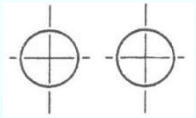
$$m = m_0 / \sqrt{(1-(v/c)^2}$$

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

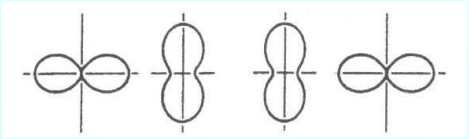
$$E = -(2\pi^2 e^4 / n^2 h^2) m Z^2,$$



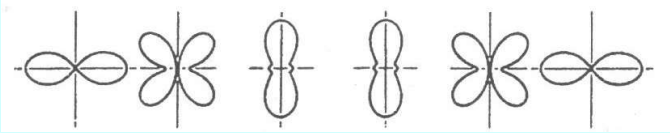
- contraction and stabilization of $s_{1/2}$ and $p_{1/2}$ orbitals



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

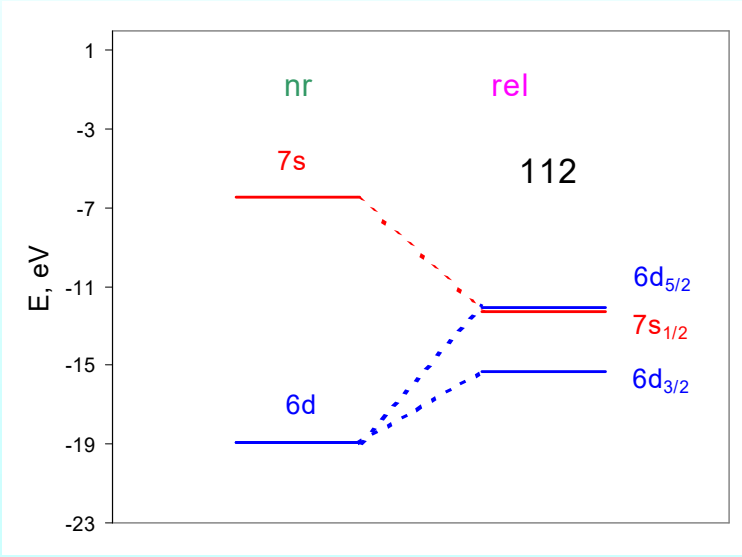


$d_{5/2}$ orbitals

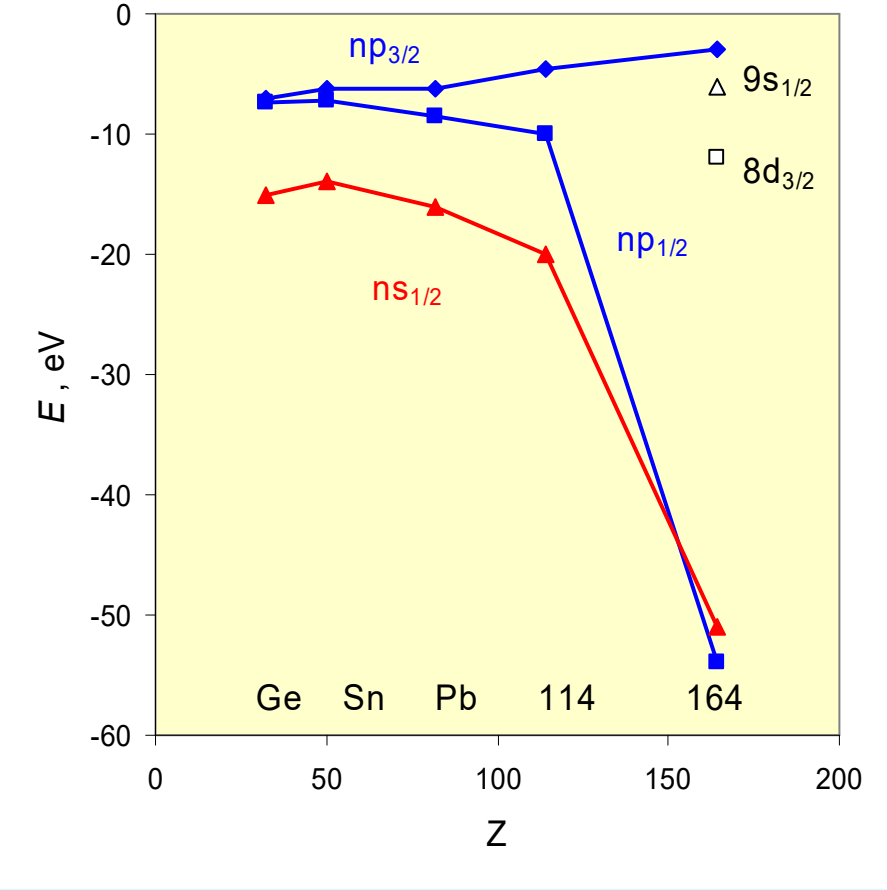


- SO splitting of p, d, f orbitals: $j = l \pm s$

scale as ~ Z^2



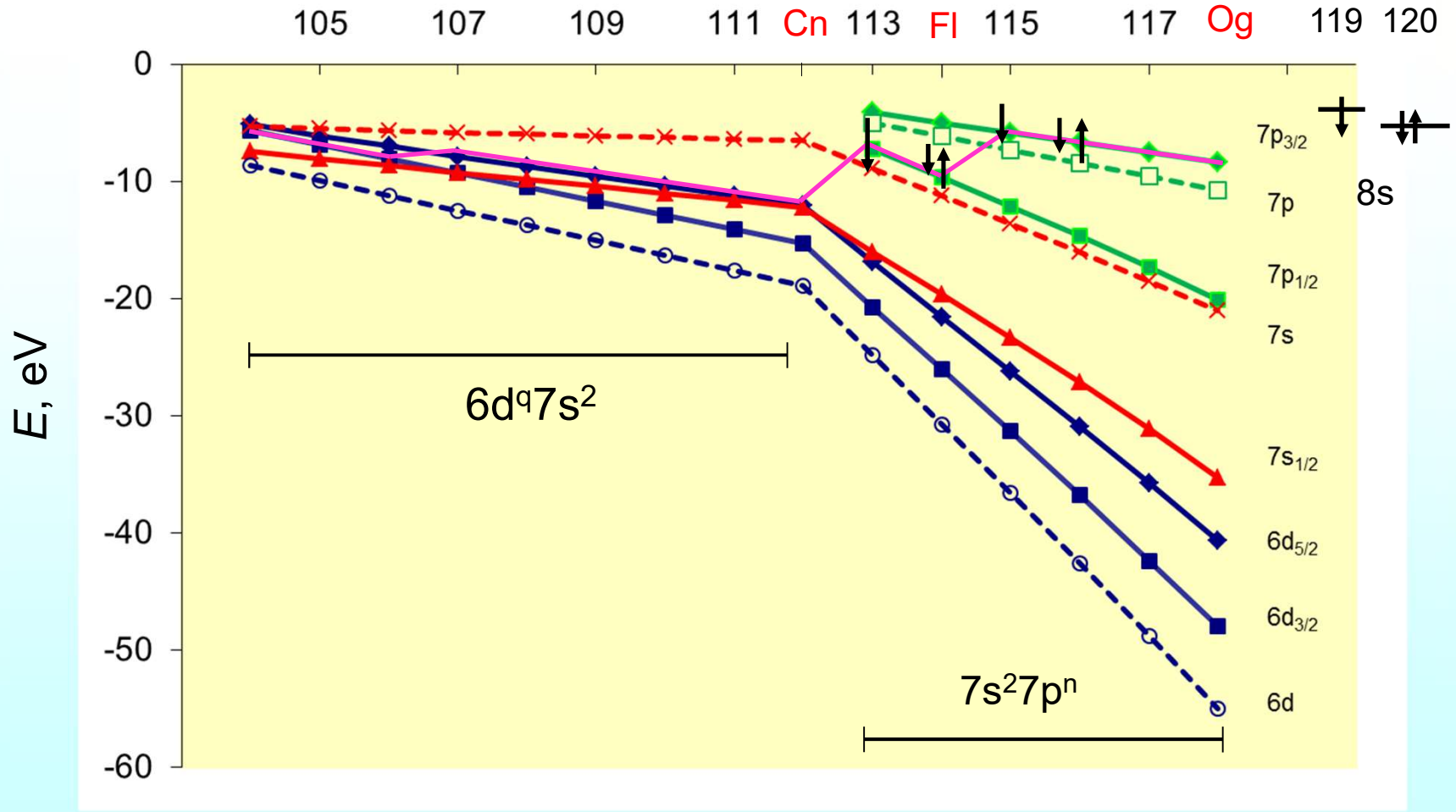
Trends in the ns and np AO Energies



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

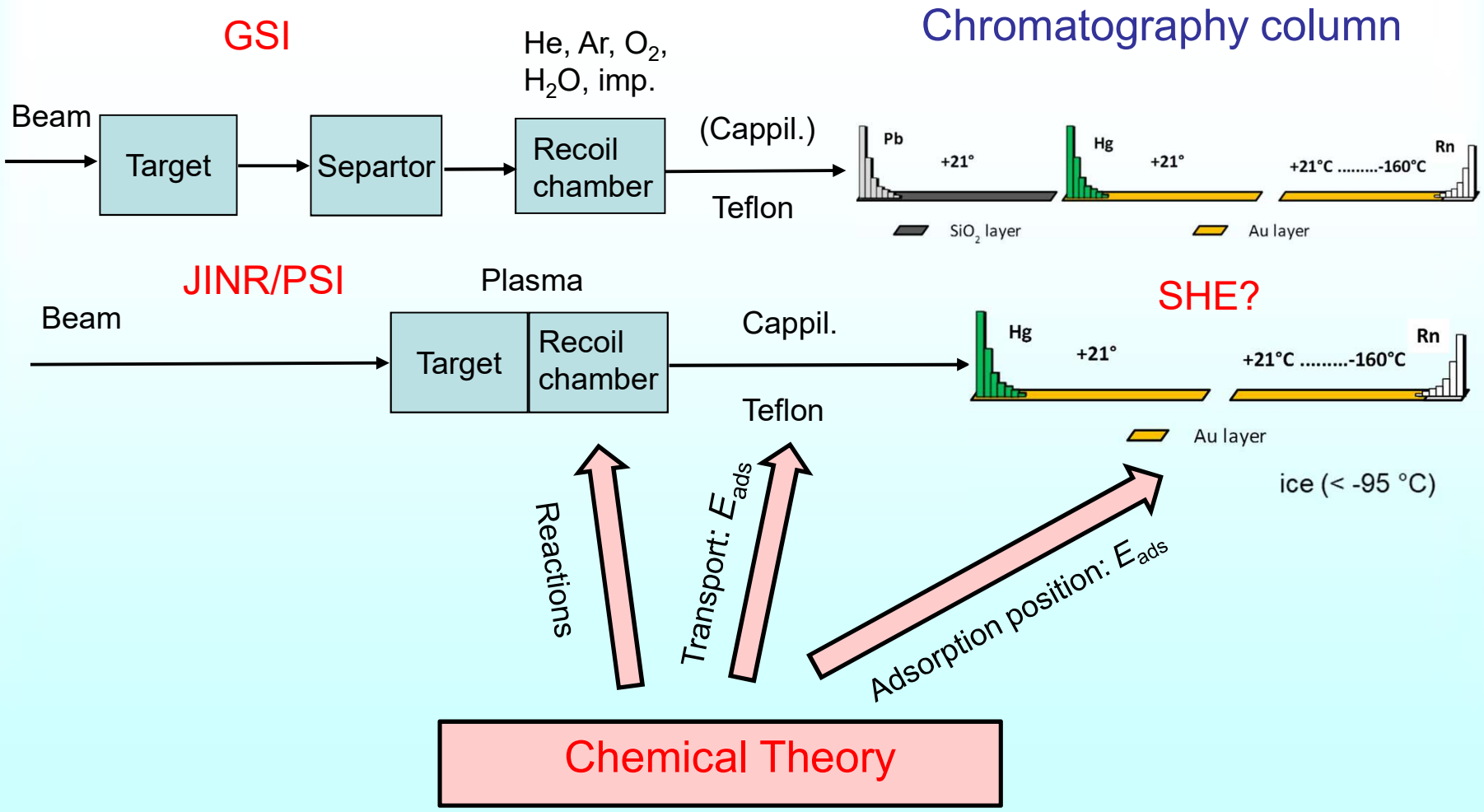
Relativistic and Nonrelativistic Energies of Valence AOs

E119 = - 4.3 eV
E120 = - 5.2 eV



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

Gas-Phase Chromatography Experiments on SHEs



Theoretical Tasks

- Predictions of atomic properties
  - Production (for calculations of mean charge of heavy ions moving in a gas - for gas-filled separators)
  - Transport through capillaries for chemical experiments (intreraction with Teflon, PE)
- Predictions of chemical properties and reactivity
  - Reactions is the gas phase
  - Adsoprtion on metal (Au) and non-metal (Si_3N_4, quartz, ice) surfaces of the chromatography column

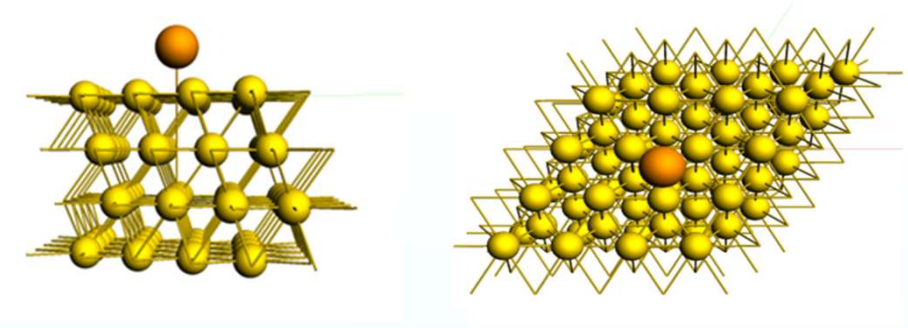
Methods and Software

- Atomic
  - DIRAC (2c/4c-DFT + CC – *ab-initio*; all electron)
  - Tel Aviv code (E. Eliav, *et al*)
- Molecular
  - ADF (SCM)
    - 2c-DFT; all-electron; geometry optimization, STO basis sets for SHEs
    - *commercial & host-locked*
  - DIRAC
    - 2c/4c-DFT + CC – *ab-initio*; all electron, Gaussian orbitals; poor geometry optimization, *free-of-charge*
- Solid state – (DFT) periodic
  - SCM BAND
    - 2c-SR and SO relativity, all electron, fast geometry optimization, full relaxation, dispersion-corrected E^{xc} , -*commercial & host-locked*
  - VASP – Pseudo Potentials

$$E[\rho] = T_s[\rho] + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) + E_{\text{H}}[\rho] + E_{\text{xc}}[\rho],$$

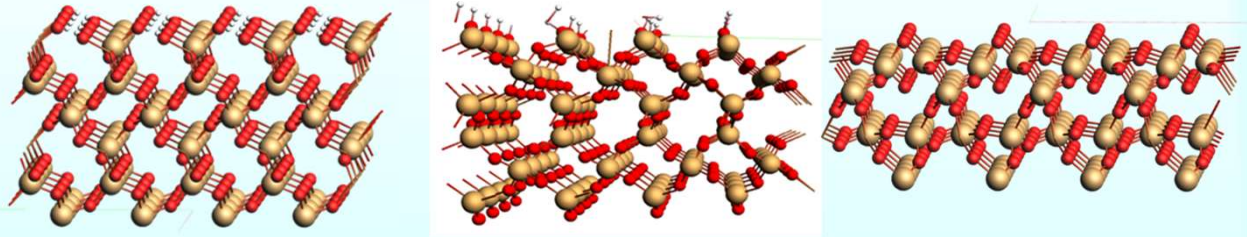
Modeling of Gold and Quartz Surfaces

- Au(111)

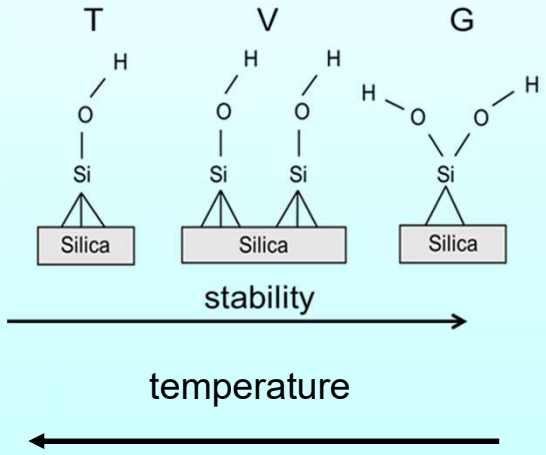


room T

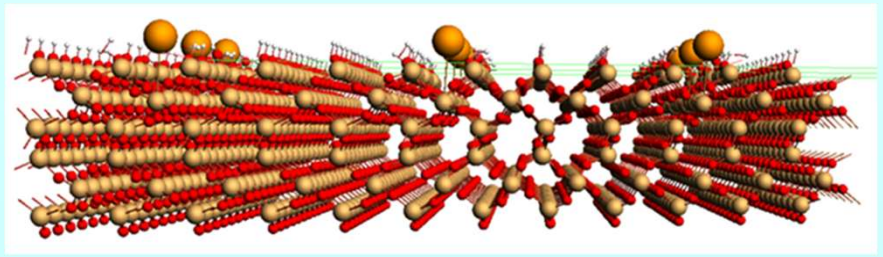
- Quartz



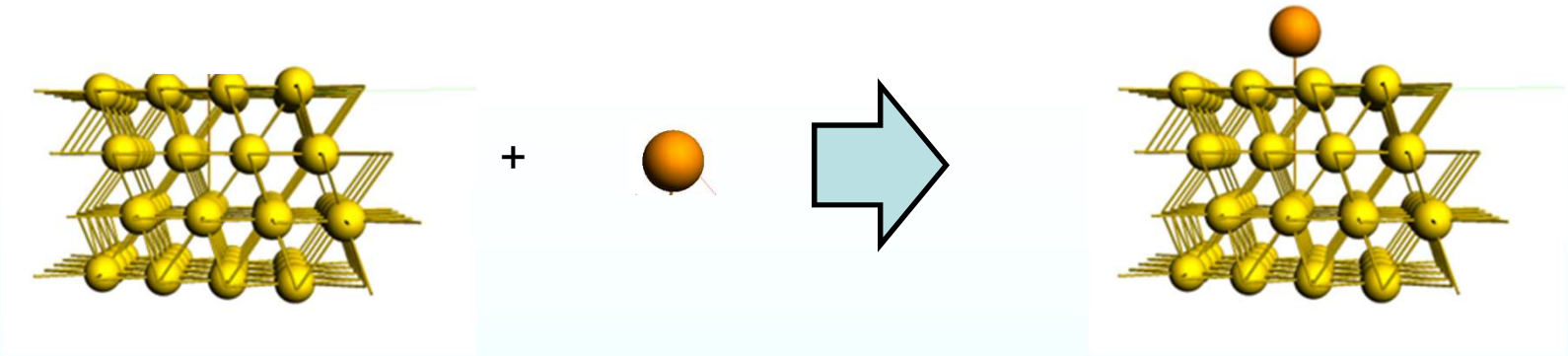
geminal vicinal (80%) bridged



(4 x 4)
supercell

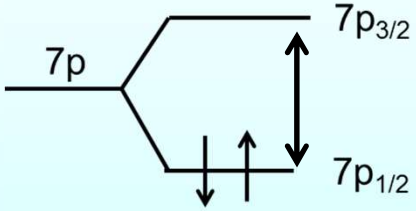


ADF BAND Calculations of E_{ads} of M on Au(111) Surface

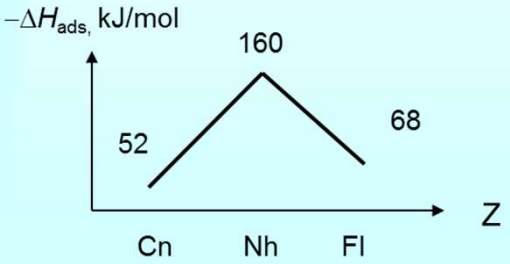


$E_f(Au_{sc})$ E_f (M-atom) $E_f(M\text{-}Au_{sc})$

Fl

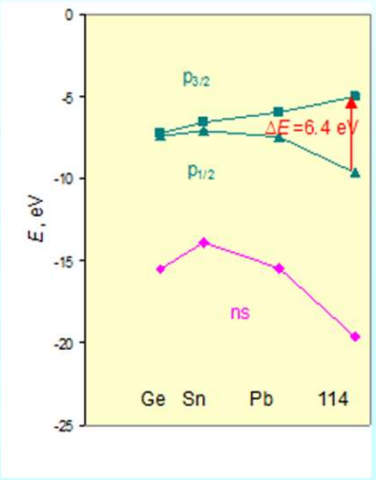


SO

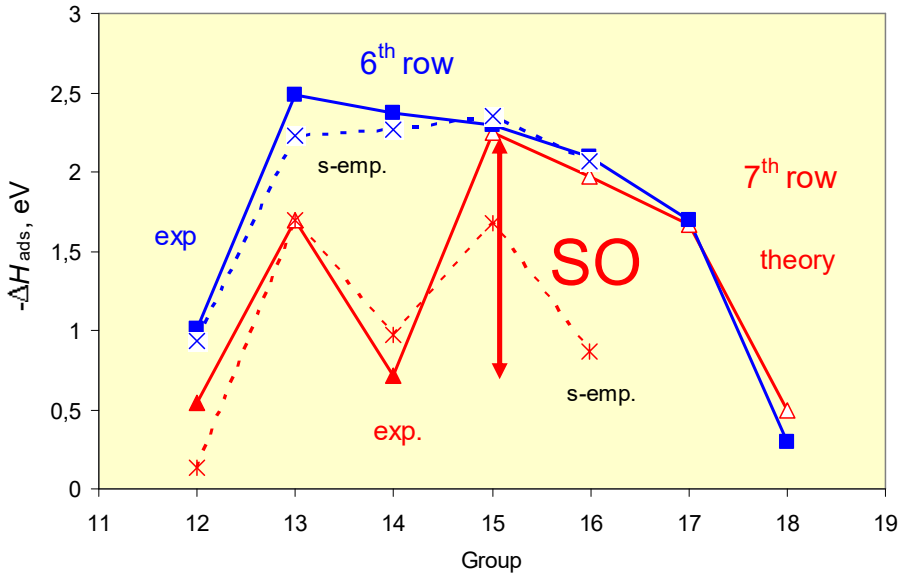


$E_{ads} = - E_f[M\text{-}Au_{sc}] - E_f(M) - E_f[Au_{sc}]$

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

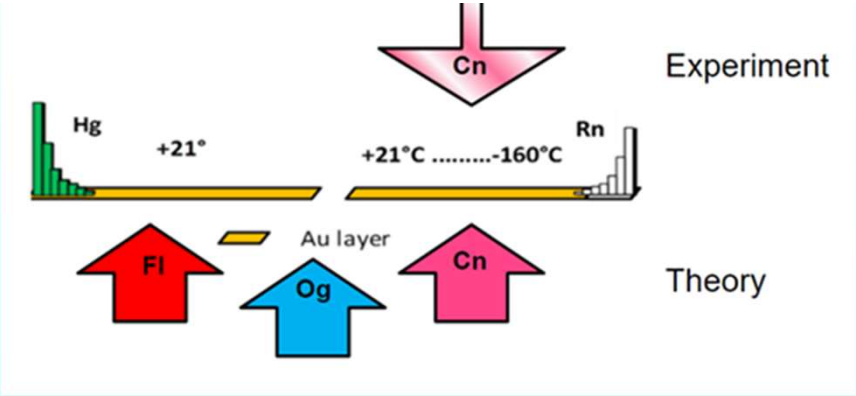


Adsorption of SHEs on the Au(111) Surface



-ΔH_{ads} on gold, kJ/mol

Element	theory	exp.
Cn	45	52
Nh	159	-
Fl	86	35, > 52
Mc	217	~~Fl~~ and FlO_2 ?
Lv	190	-
Ts	161	-
Og	78	-
	70 (Tr)	



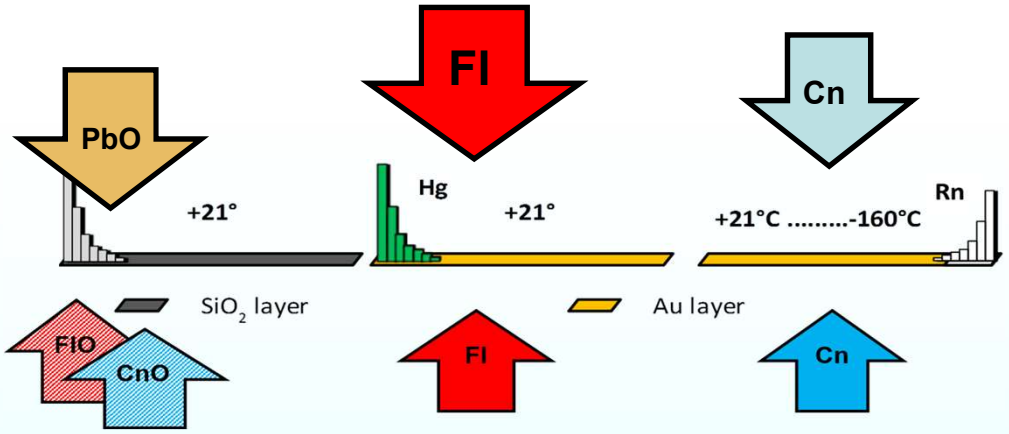
V. Pershina, *et al*. JCP, **133**, 104304 (2010)

A. Rhyzkov, V. Pershina, *et al.* PCCP, **25**, 15362 (2023)

L. Thrombach, *et al*. PCCP, **21**, 18048 (2019)

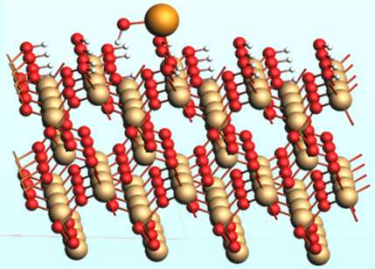
Only E_{ads} of Cn, Og and Fl can me measured

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

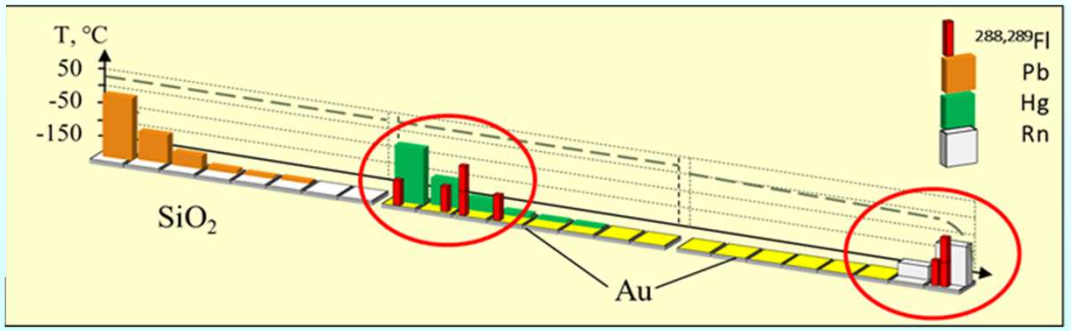


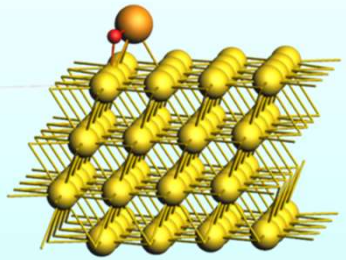
experiment

theory



quartz





Au

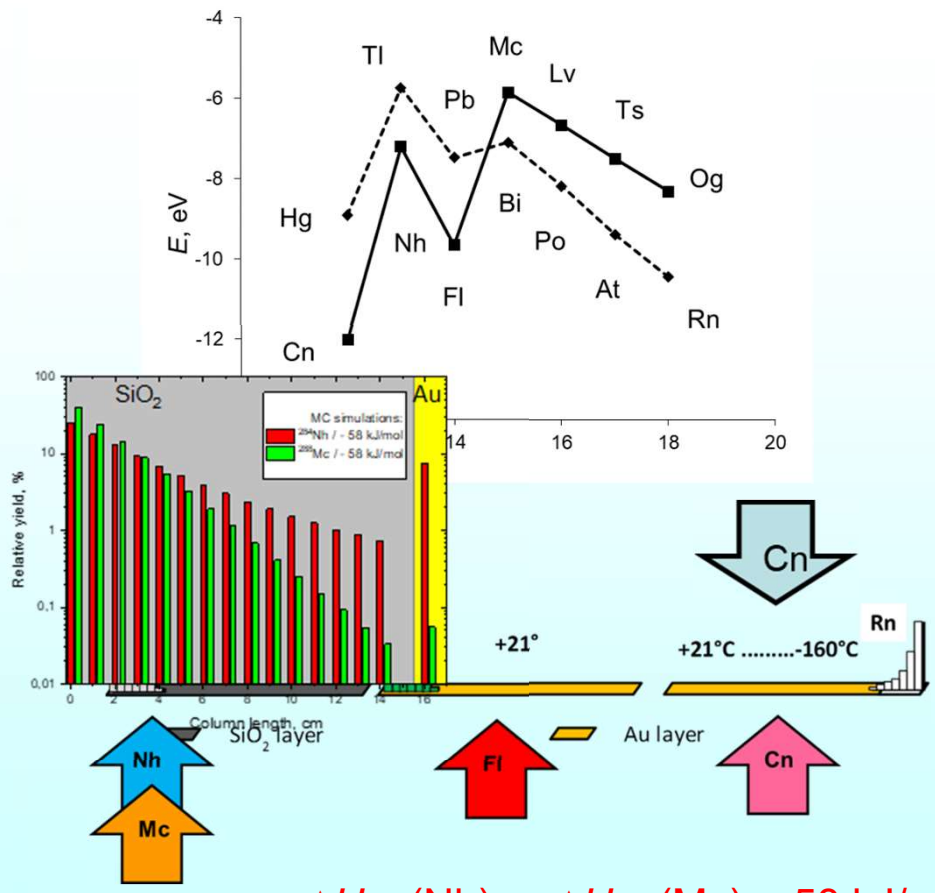
Theory: V. Pershina and M. Ilias, *Dalton Trans.* **51**, 7321 (2022)

?

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

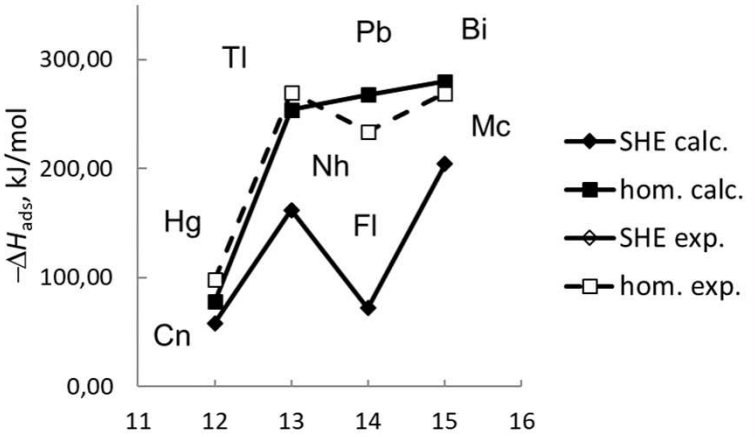
Calculations of E_{ads} of Group 12-15 Elements on Gold and Quartz

AOs



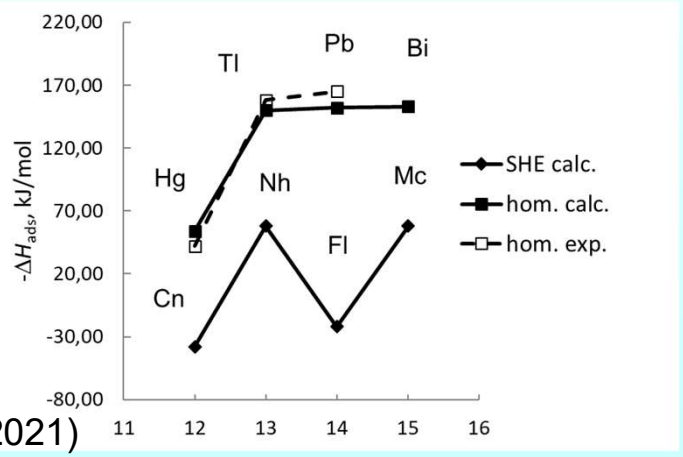
$-\Delta H_{ads}$(Nh) = $-\Delta H_{ads}$(Mc) = 58 kJ/mol

M/Gold



(revPBE-D3BJ)

M/Quartz



Theory: V. Pershina, M. Ilias, A. Yakushev, *Inorg. Chem.* **60**, 9796 (2021)
Experiment on Nh and Mc: A. Yakushev, *et al. Frontiers* (2024)

At and Ts on Quartz

MOLECULAR PHYSICS e2363408
https://doi.org/10.1080/00268976.2024.2363408

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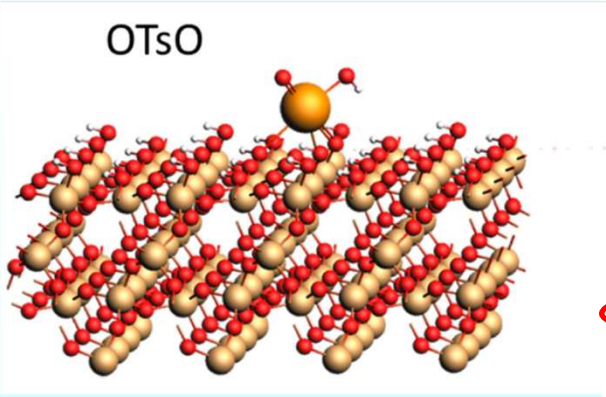
RESEARCH ARTICLE

Check for updates

Theoretical predictions of properties and adsorption behaviour of a superheavy element Ts and its lighter homolog At, and of their various gas-phase compounds, on hydroxylated quartz surfaces from periodic DFT calculations

Miroslav Iliaš [a,b] and Valeria Pershina [b]



At < Ts

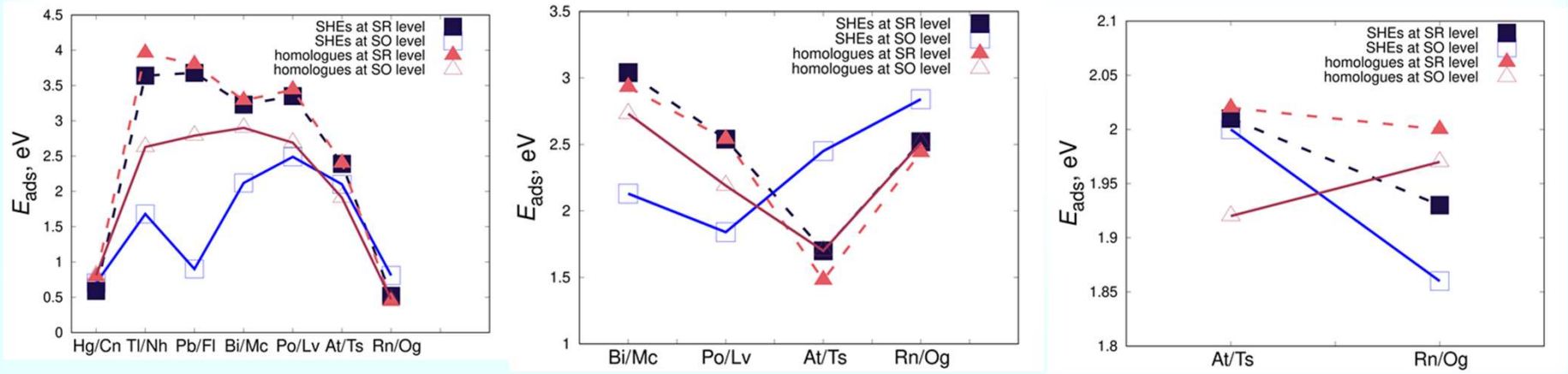
Table 9. Summary of the calculated adsorption energies of the At and Ts species on the Q(G) and Q(V) surfaces in comparison with experimental $-\Delta H_{ads}$ (in kJ/mol). (The radicals are marked with a star).

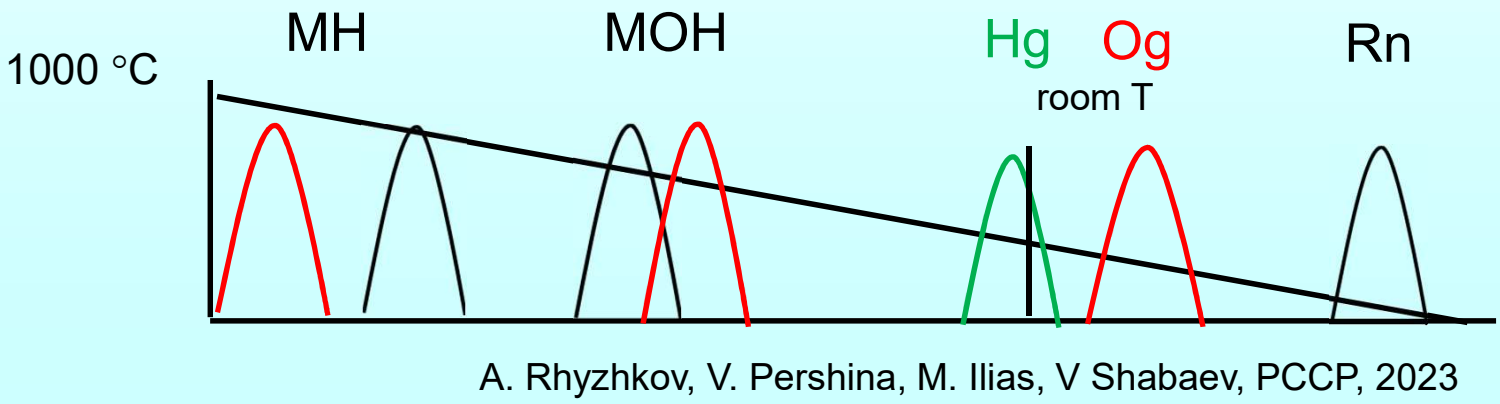
Adsorbed species	At				Ts	
	Theory		Experiment		Theory	
	Q(G)	Q(V)	Quartz	Conditions	Q(G)	Q(V)
M	26	20	123 ± 10^{a}	H_2	23	20
MH	31	41			32	48
MOH	36	42	47 ± 5^{a}	He/H_2O	29	47
			$< 65^{b}$	He/Ar		
MO*	39	77			105	125
MOO*	34	34	$80 \pm 5^{a,c}$	$He/O_2/H_2O$	35	49
OMO*	76	98	$80 \pm 5^{a,c}$	$He/O_2/H_2O$	135	158
OMOH	43	99			96	109
MO(OH)	59	83			52	69

Experiment: [a] A. Serov, RA (2011) ; [b] N. Chiera, Mol. Phy. (2023).

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

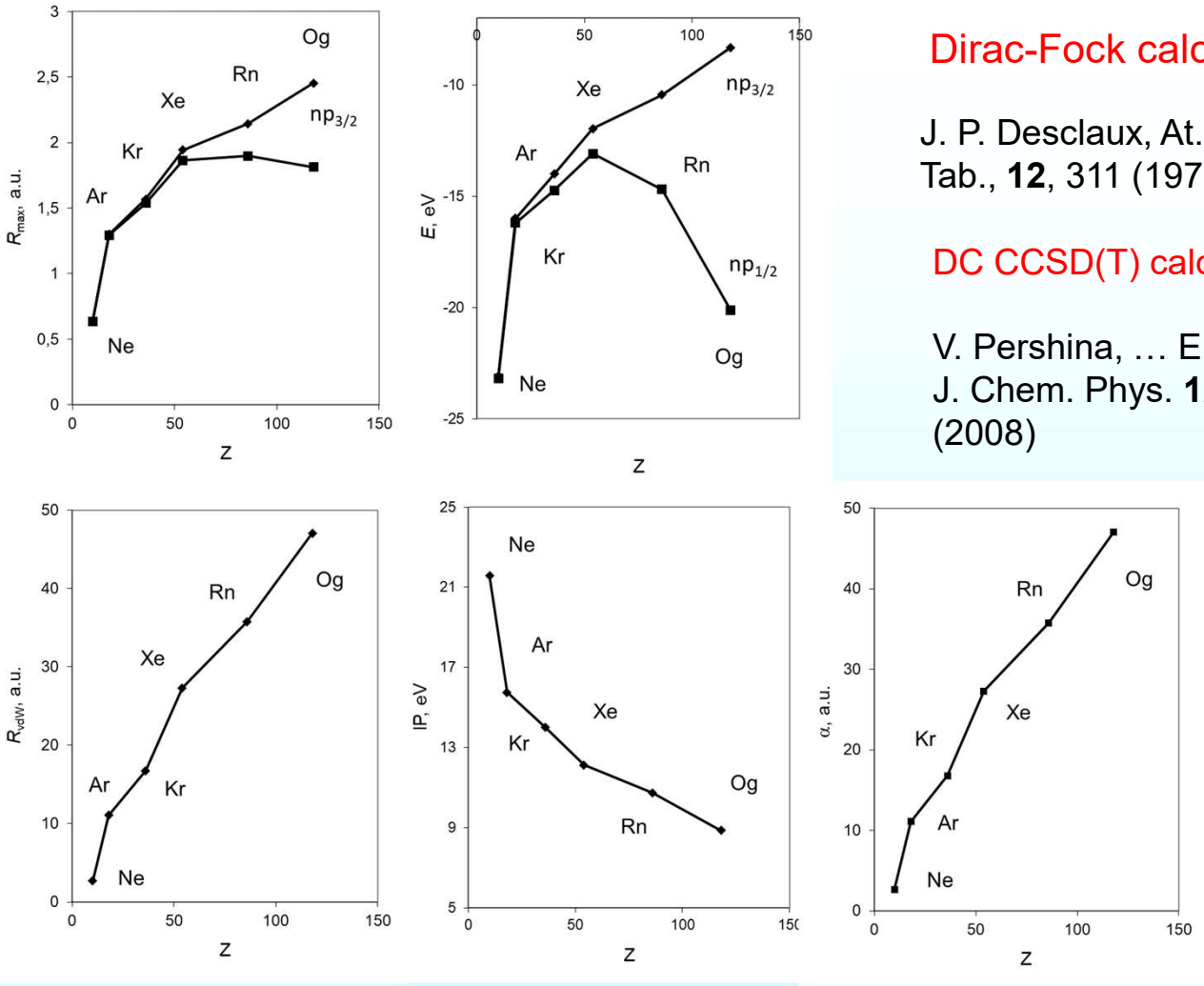
M MH MOH





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

Atomic Orbitals and Properties of Group-18 Elements: Smooth Trends



Dirac-Fock calculations:

J. P. Desclaux, At. Dat. Nucl. Dat. Tab., **12**, 311 (1973)

DC CCSD(T) calculations:

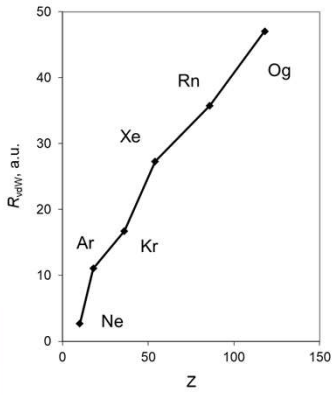
V. Pershina, … E. Eliav, *et al*, J. Chem. Phys. **129**, 144106 (2008)

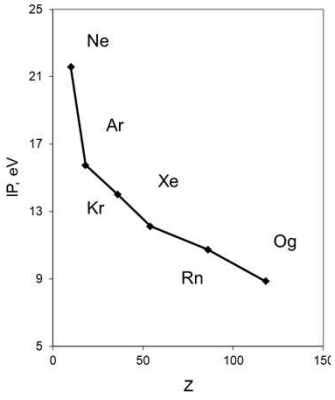
Smooth Trends in AOs: Og deviates?

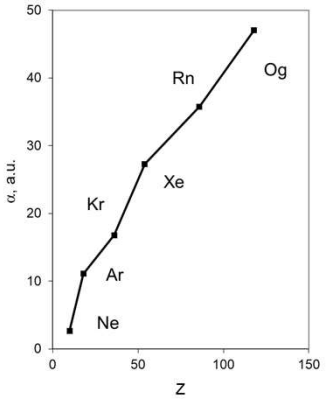
Adsorption of inert gases including element 118 on noble metal and inert surfaces from *ab initio* Dirac–Coulomb atomic calculations

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)





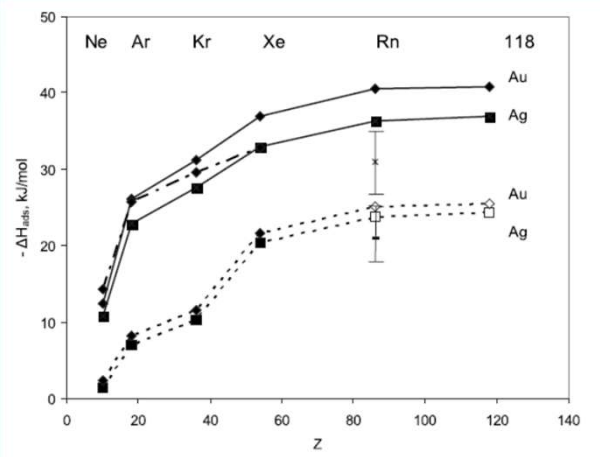


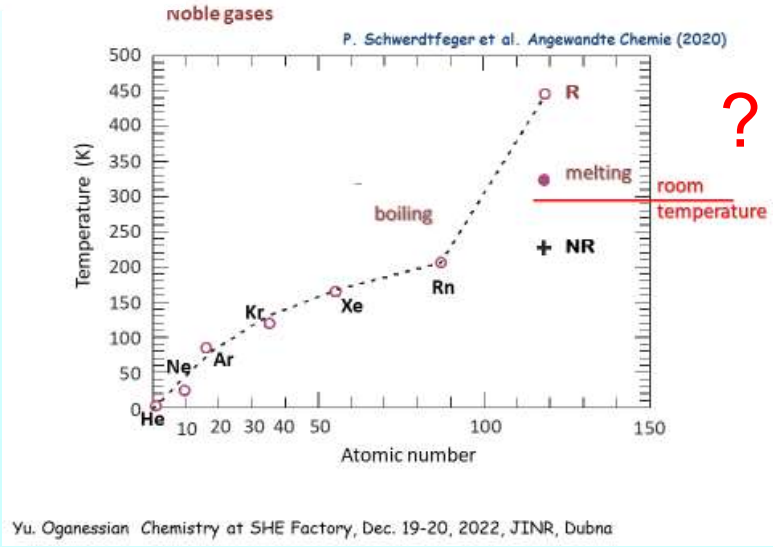
Van der Waals interaction energy

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

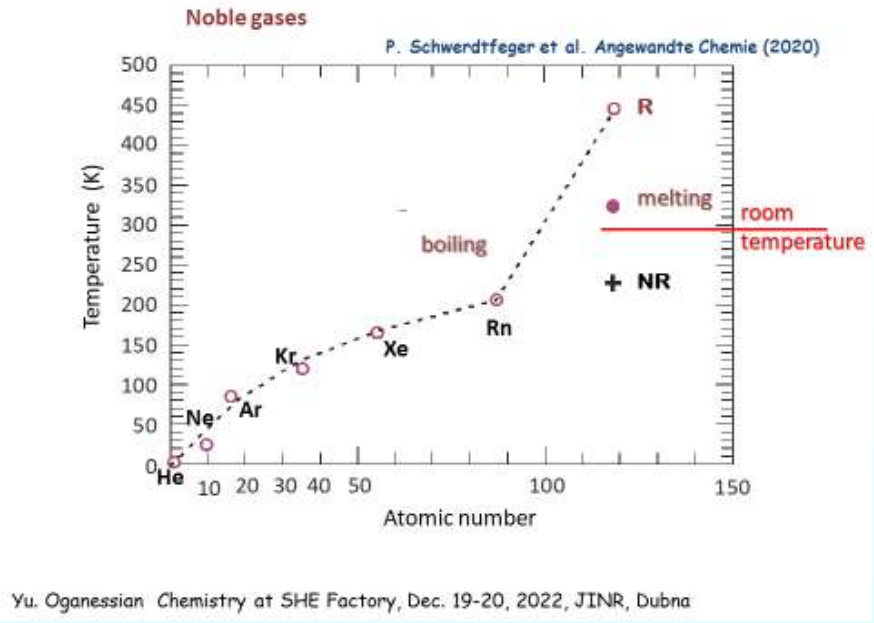
$x \approx R_{vdW}$

Physisorption on surfaces





Smooth Trends: Og is Solid?

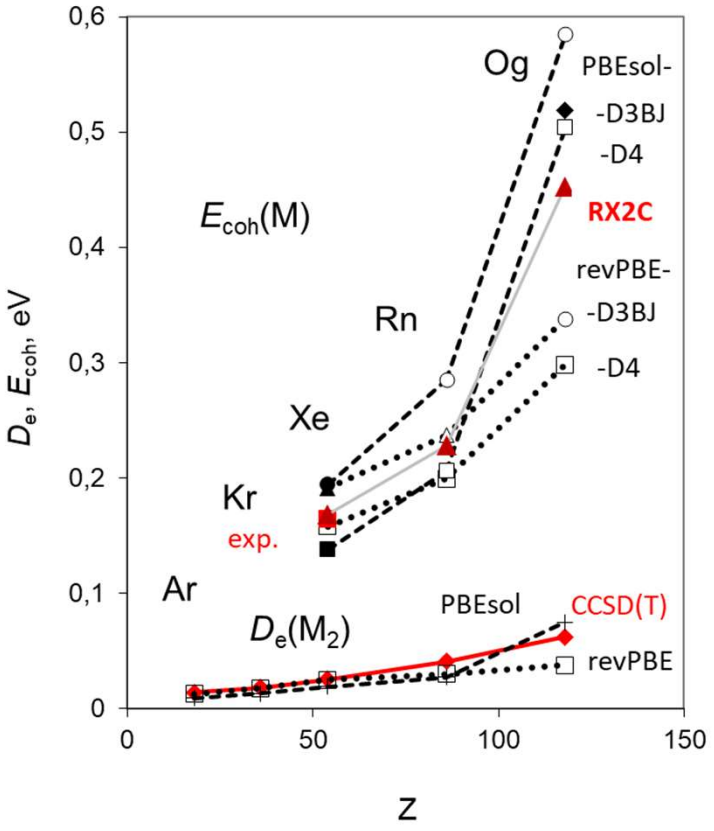


$$E[\rho] = T_s[\rho] + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) + E_{\text{H}}[\rho] + E_{\text{xc}}[\rho],$$

Exact form of exchange-correlation funtional (E_{xc}) for Og is unknown

The trend depends on E_{xc}

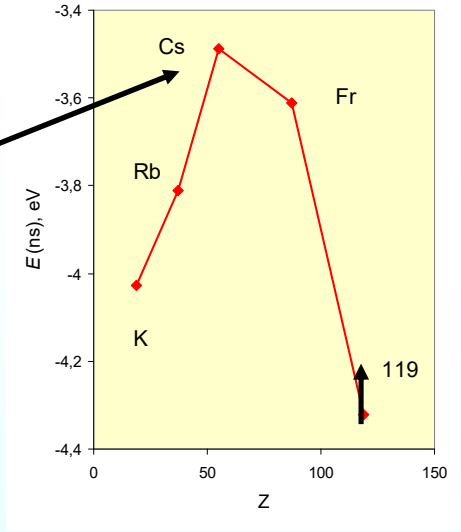
(A. Ryzhkov, Ch. Tandardini, *et. al.*, preliminary)

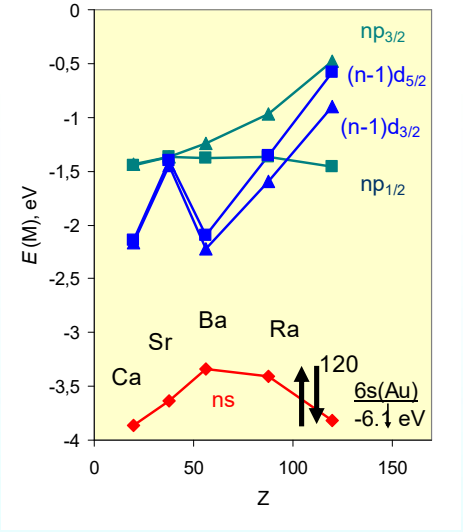


(RX2C: P. Jerabeck, et al.
J. Phys. Chem. 123, 4201 (2019))

Atomic Orbitals of Group-1 (ns^1) and Group-2 (ns^2) Elements

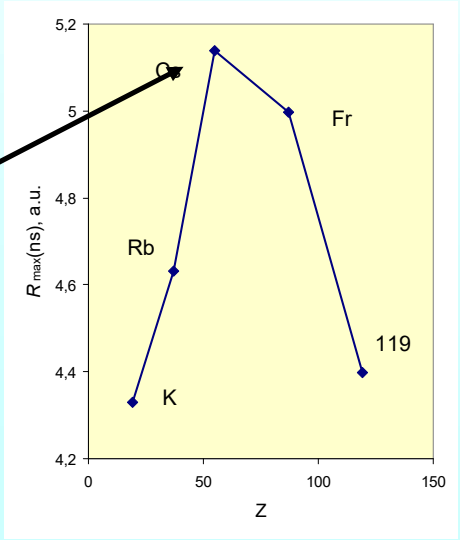
. 4s
.
. 6s
.
. 8s

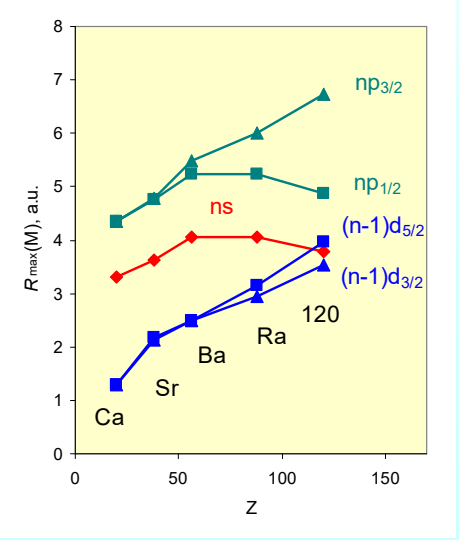




A reversal of trends

. 4s
.
. 6s
.
. 8s





Theory Studies on Elements 119 and 120

- A. Borschevsky, V. Pershina, E. Eliav, and U. Kaldor, *J Chem. Phys.* **138**, 124302 (2013). *Ab initio* studies of atomic properties and experimental behaviour of element 119 and its lighter homologs.
- A. Borschevsky V. Pershina E. Eliav and U. Kaldor, *Phys. Rev.* A **87**, 022502 (2013). *Ab initio* predictions of atomic properties of element 120 and its lighter group-2 homologues.
- V. Pershina, A. Boschevsky, J. Anton, Fully relativistic study of intermetallic diners of group-1 elements and predictions of their adsorption properties. Chem. Phys. **395**, 87 (2012).
- V. Pershina, A. Borschevsky, J. Anton, Theoretical predictions of properties of group.2 elements including E120 and their adsorption on noble metal surfaces, J. Chem. Phys. **136**, 134317 (2012)
- **Theoretical predictions of properties and adsorption behavior of group 1 and 2 elements, including elements 119 and 120, on the surface of gold from periodic DFT calculations** (2023)

  Valeria Pershina [a] and Miroslav Iliaš [a,b,c]

  MOLECULAR PHYSICS e2237614
  https://doi.org/10.1080/00268976.2023.2237614

  REHE 2022 SPECIAL ISSUE
- **Theoretical predictions of properties and adsorption behaviour of group 1 and 2 elements, including elements 119 and 120, on hydroxylated quartz surfaces from periodic DFT calculations** (2023)

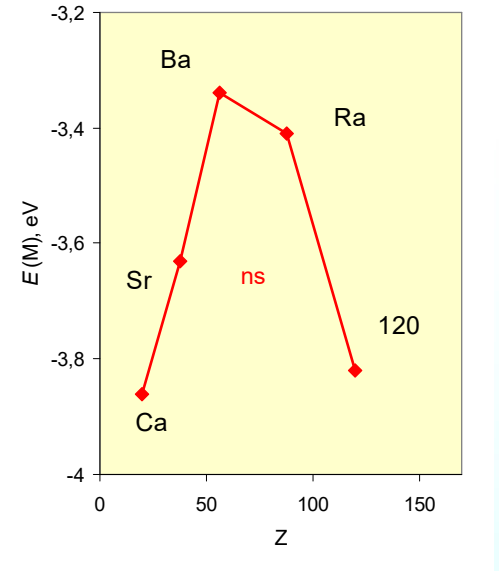
  Miroslav Iliaš [a,b,c] and Valeria Pershina [c]

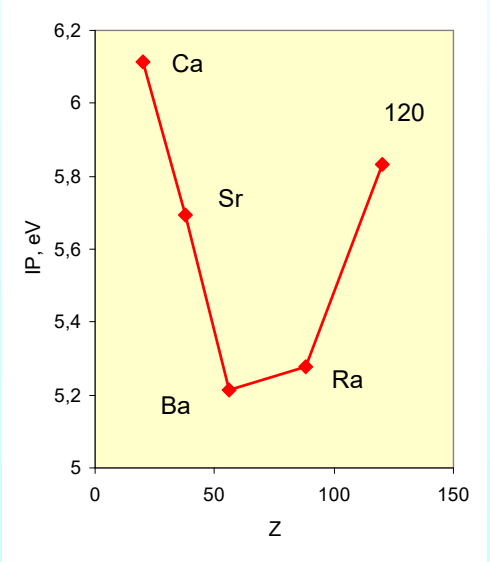
  MOLECULAR PHYSICS e2293229
  https://doi.org/10.1080/00268976.2023.2293229

Ionization Potentials and Electron Transitions

IPs (in eV) and EE (in cm^{-1})

Element	IP/E	To state	XIHFSCC (present)	CI+MBPT (Dinh)	Exp.
Ra	IP1	$7s^1$ (^2S)	5.283	5.274	5.279
			5.277 (QED)		
	IP2	$7s^0$ (^1S)	10.177	10.172	10.148
120	IP1	$7s^1$ (^2S)	5.851	5.864	-
			5.838 (QED)		
	IP2	$7s^0$ (^1S)	11.137	11.150	-
	EE	8s8p ($^3P_0$)	15648	15777	-
		7d8s ($^3D_1$)	22903	22985	
		....	...	...	
		8s9p ($^3P_2$)	37369	-	-

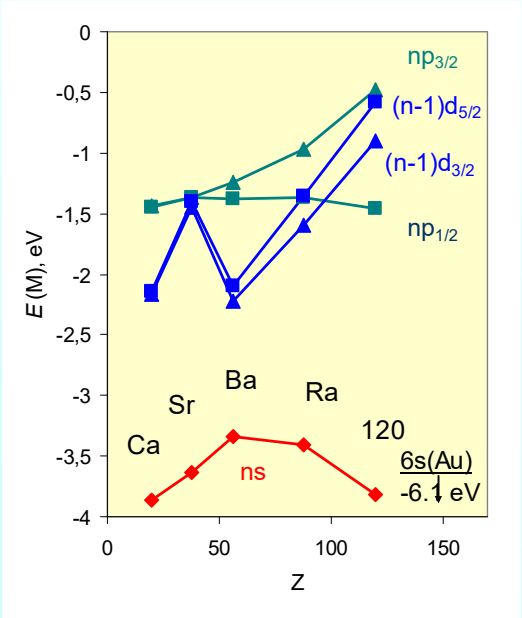


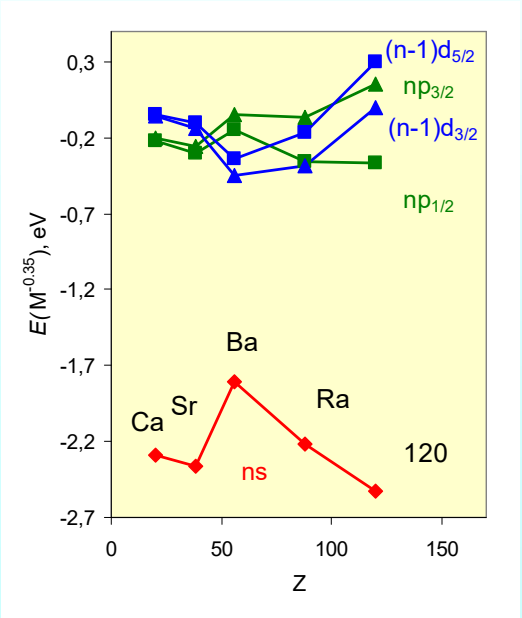


Calculations of EAs

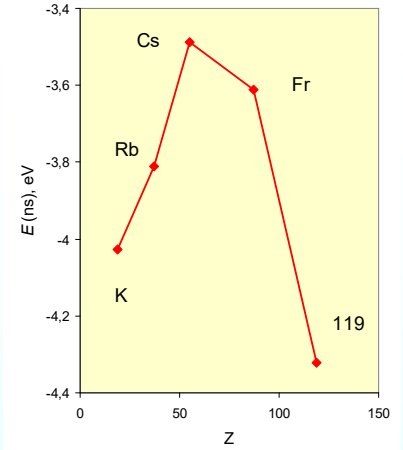
Electron Affinities (in meV)

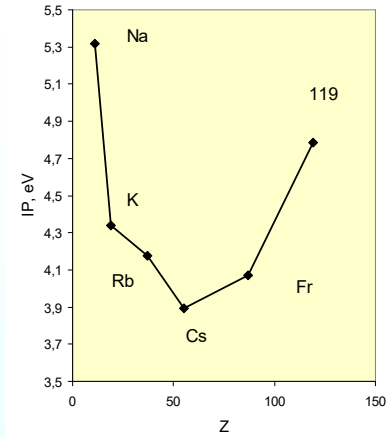
Elem.	State	DHF	RCCSD	RCCSD(T)	Exp.
Ba^-	$6s^26p\ (^2P)$	-0.143	0.070	0.138	0.144
Ra^-	$7s^27p\ (^2P)$	-0.099	0.042	0.082	
120^-	$8s^28p\ (^2P)$	-0.121	-0.002	0.021	-

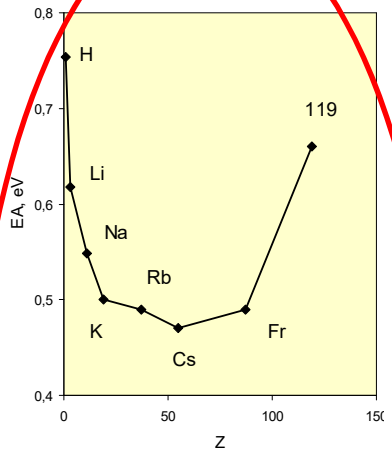


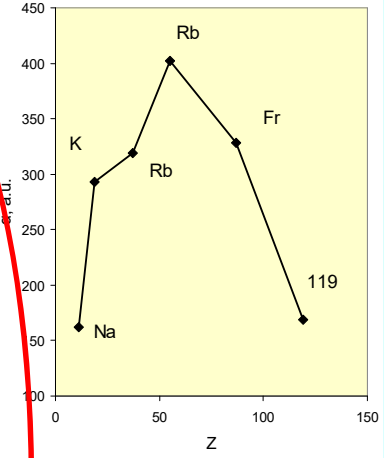


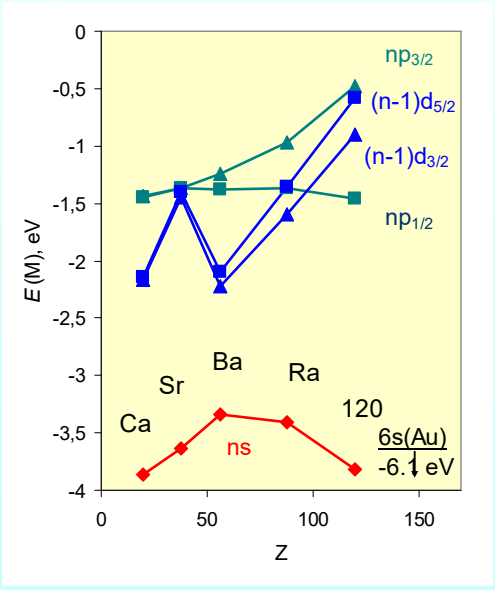
Atomic Properties of Group-1 and 2 Elements

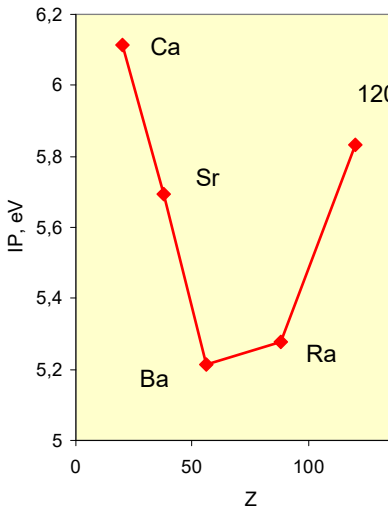


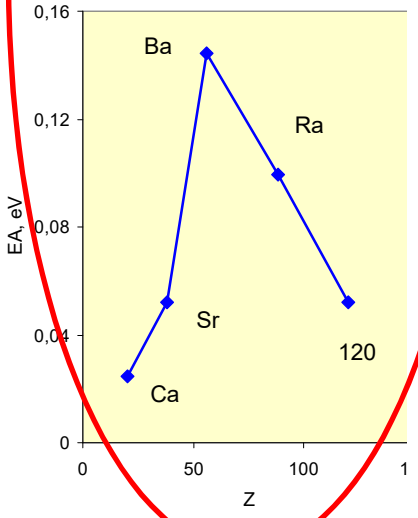


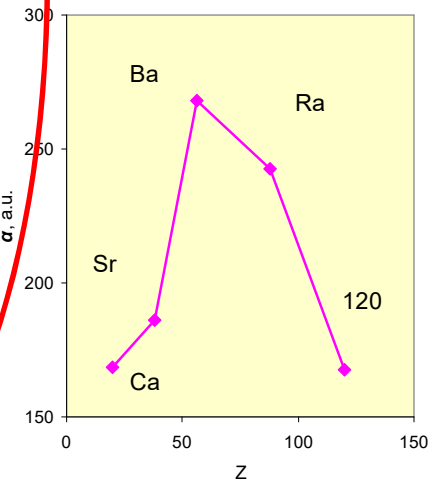








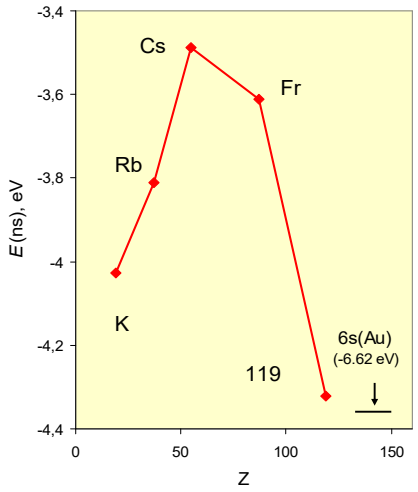


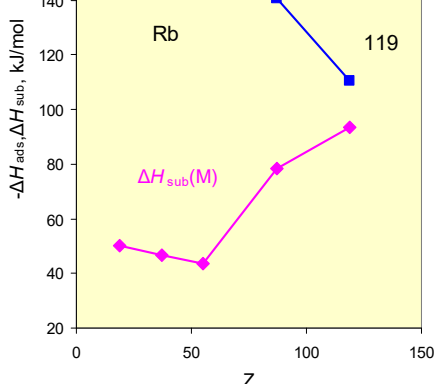


Sublimation and Adsorption of Group-1 and 2 Elements

$-\Delta H_{ads}/\Delta H_{sub}$

Group 1: ns^1

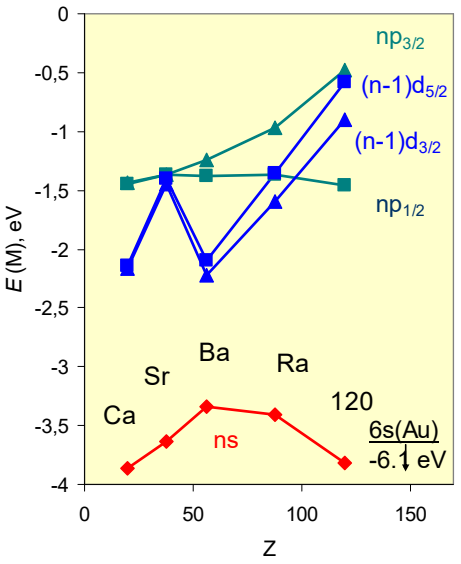


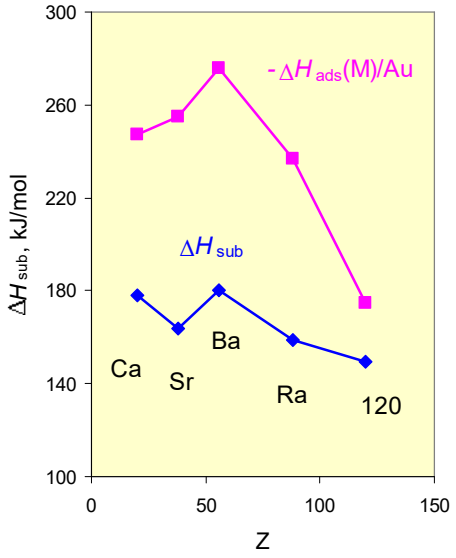


ionic bond

covalent bond

Group 2: ns^2





ionic bond

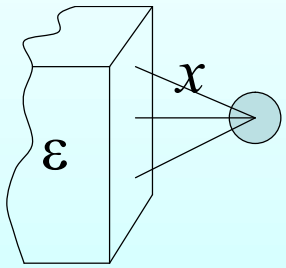
vdW bond

Predictions of Transportation of E120

- Relative yield after a capillar

$$\frac{N}{N_0} = e^{-\lambda t} = e^{-\frac{\ln 2}{T_{1/2}} t_R} \qquad t_R = \frac{l a_l}{Q} \frac{u}{4} \tau_0 e^{-\frac{E}{k^B T_C}}$$

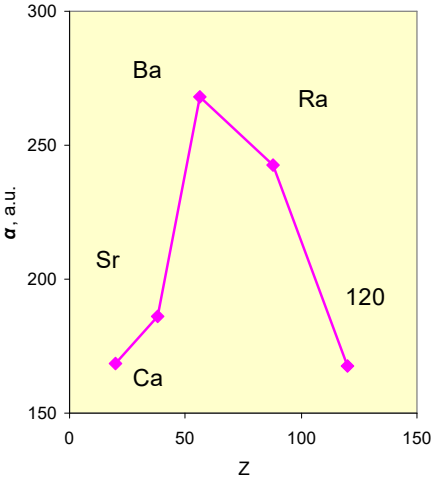
- Adsorption model

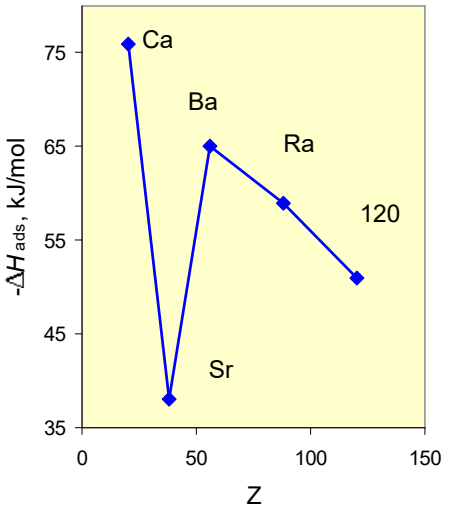


$$E(x) = -\frac{3}{16}\left(\frac{\varepsilon - 1}{\varepsilon + 2}\right) \frac{\alpha_{at}}{\left(\frac{1}{IP_{slab}} + \frac{1}{IP_{at}}\right) x^3}$$

For: $T_{1/2}$ = 1 s; T_C = 25 °C; l = 1 m

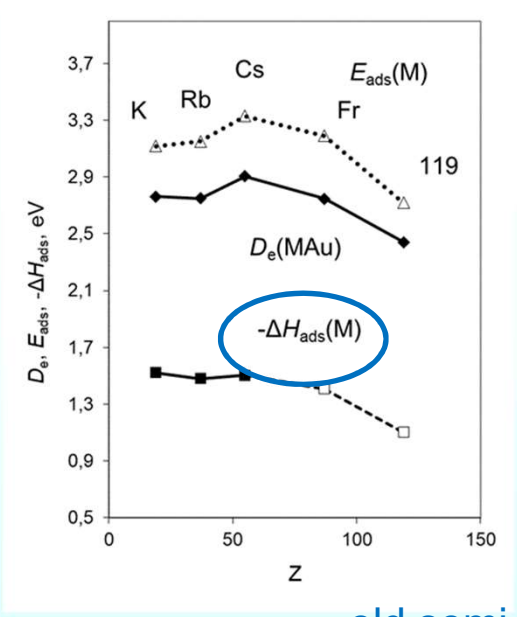
N/N_0 = 77 %

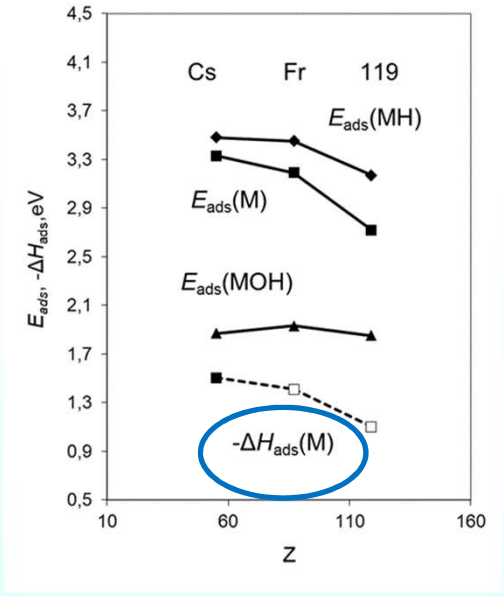


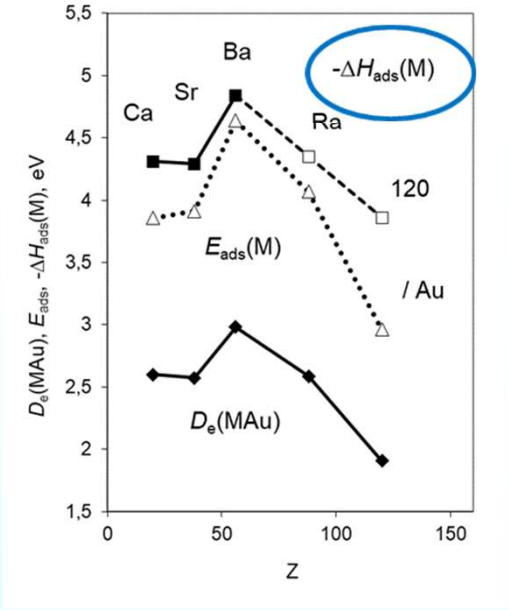


(51 kJ/mol)

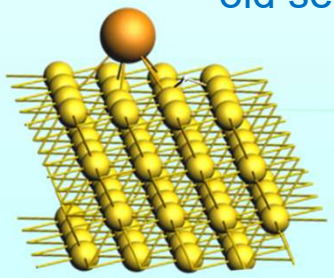
Periodic Calculations of E_{ads} of E119 and E120 on Gold Surface



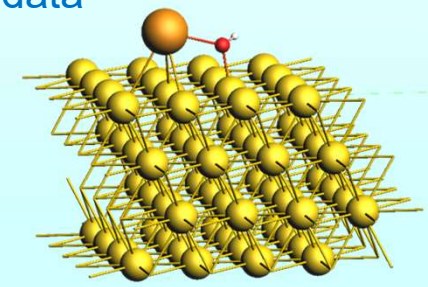




old semi-emp. data



MH



MOH

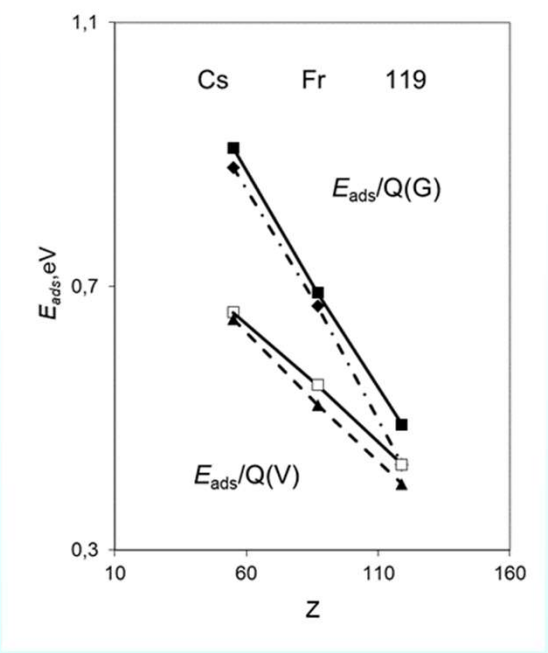
E_{ads}(119) = 260 kJ/mol

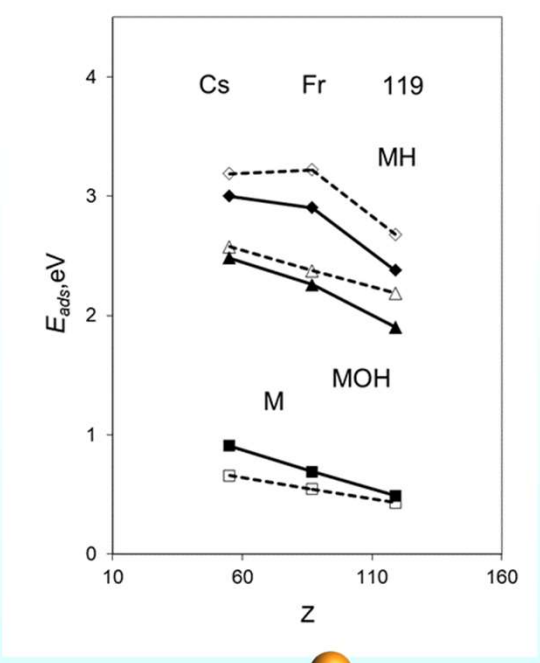
E_{ads}(119OH) = 185 kJ/mol

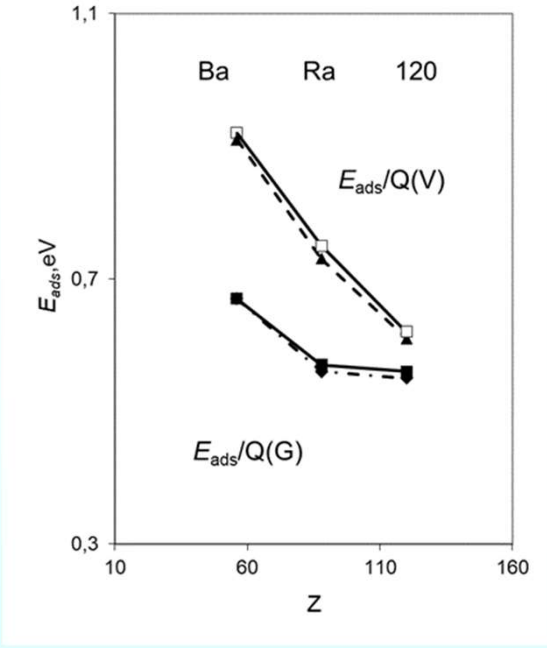
E_{ads}(120) = 286 kJ/mol

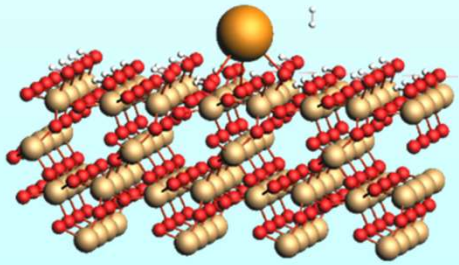
V. Pershina, M. Ilias, Mol. Phys. (2023)

Periodic Calculations of E_{ads} of E119 and E120 on Quartz Surface

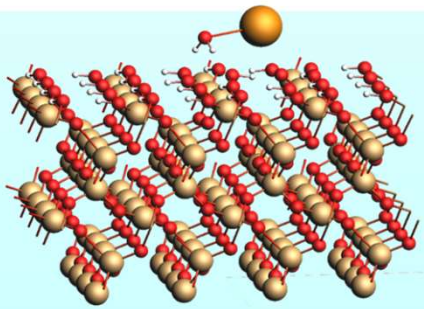








MH



MOH

E_{ads}(119) = 50 kJ/mol
Eads(119OH) = 211 kJ/mol

E_{ads}(120) = 60 kJ/mol

M. Ilias, V. Pershina, Mol. Phys. (2024)

Conclusions

- RE are important for Nh ($7p_{1/2}$) and Fl ($7p_{1/2}^2$) making them more inert
- RE on Mc-Og ($np_{3/2}^n$) are not spectacular, trends are a smooth prolongation from the lighter elements
  - Og should be similar to Rn, noble gas (?)
  - Og should adsorb on gold and can be detected by present techniques
- RE on E119 (ns^1) and E120 (ns^2) are spectacular due to the contraction and stabiliztaion of the ns AO, a reversal of trends in the groups from the 6th row
  - $E120^-$ is stabilized by the electron correlation
  - E_{ads} of E119 and E120 on gold are very high
  - E_{ads} on quartz are low and can be meaured by the present techniques

Thank you for your attention !