Adsorption of Superheavy Element Atoms and Molecules on Different Surfaces

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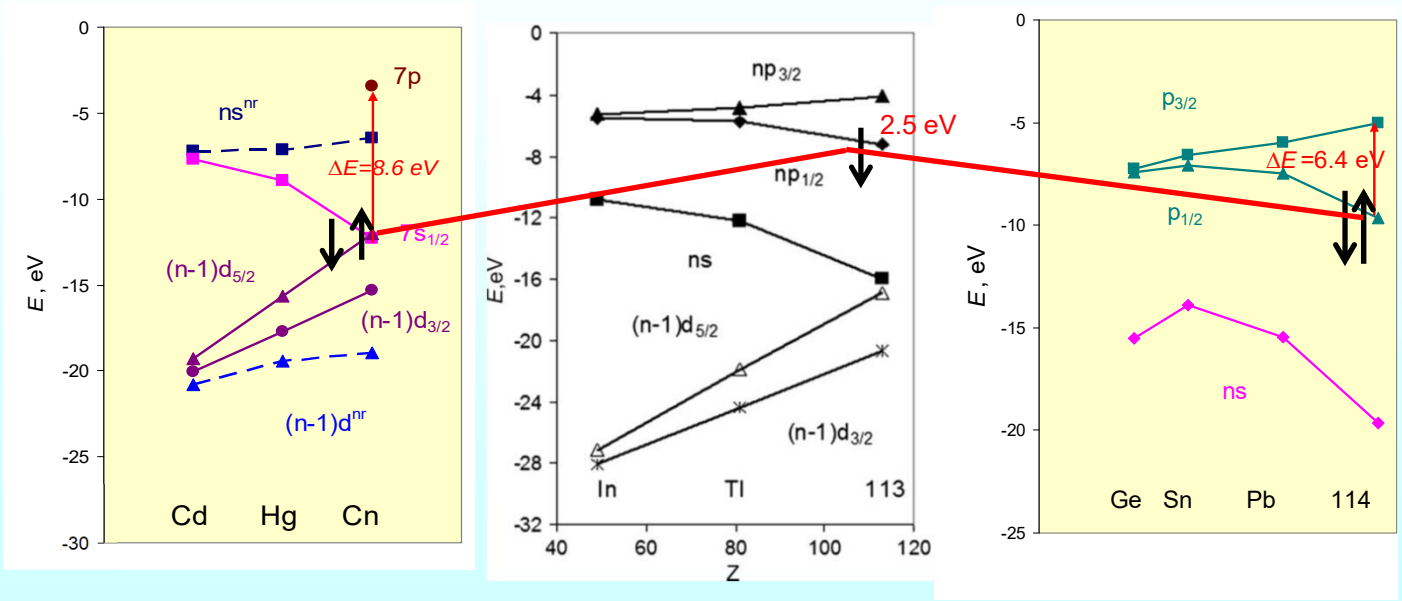
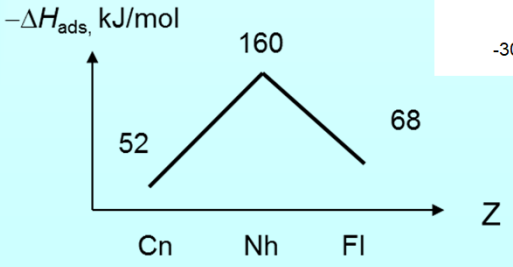
Chemical Properties of Cn, Nh and Fl

How reactive are Cn, Nh, and Fl? ΔH_{ads}?

Cn ($6d^{10}7s^2$) Nh ($7s^27p_{1/2}$) Fl ($7s^27p_{1/2}^2$)



$\Delta H_{ads}^{Au}(M)$

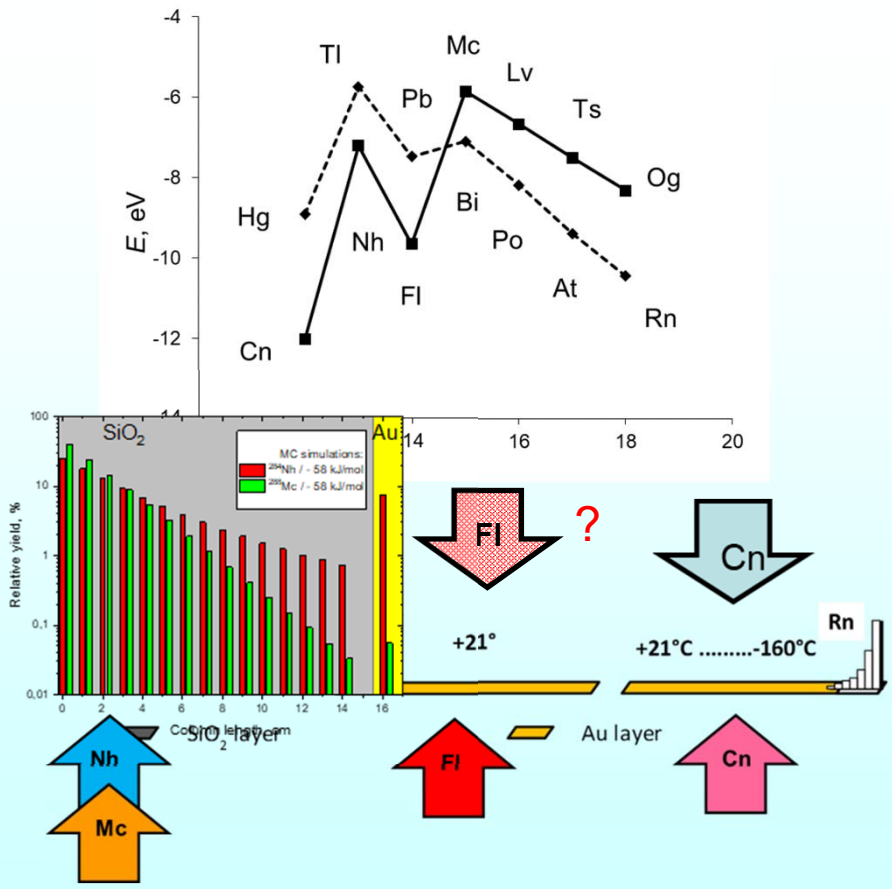


V. Pershina, *Radiochim. Acta* **107**, 833 (2019)

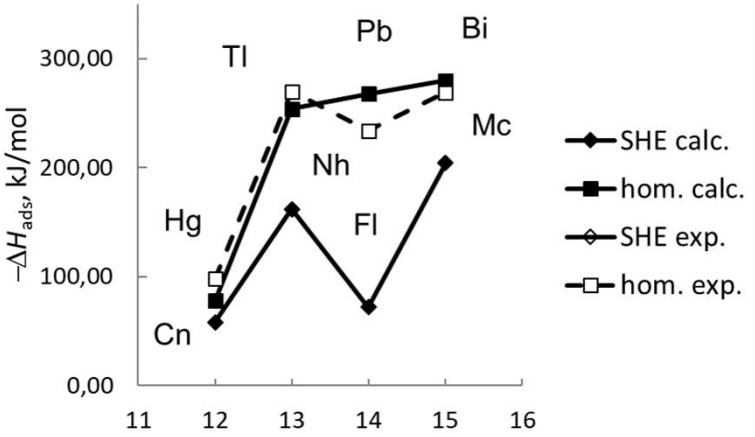
V. Pershina and M. Iliaš, 19th TASCA Workshop, May 10-12, 2022

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

Atomic Orbitals

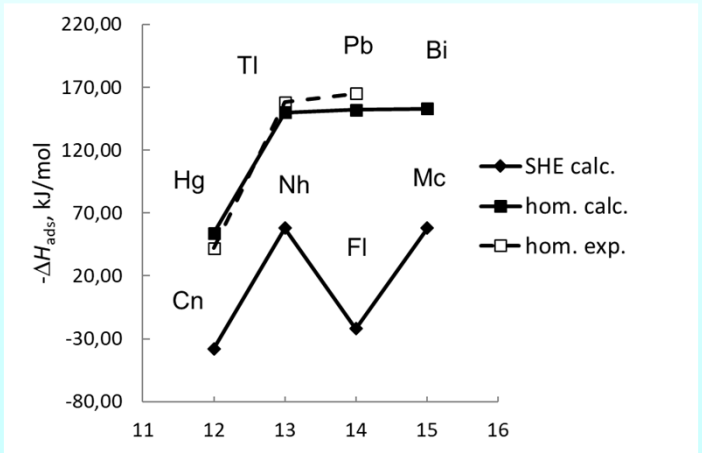


Gold



(revPBE-D3BJ)

Quartz

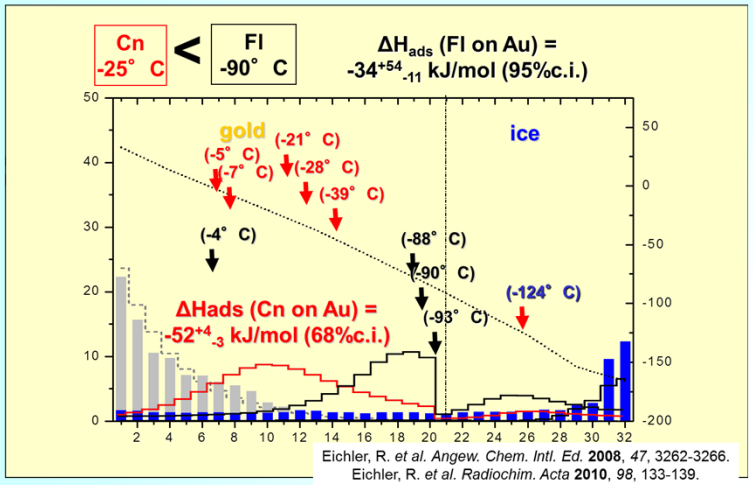


V. Pershina. M. Ilias, A. Yakushev, *Inorg. Chem*. **60**, 9796 (2021)

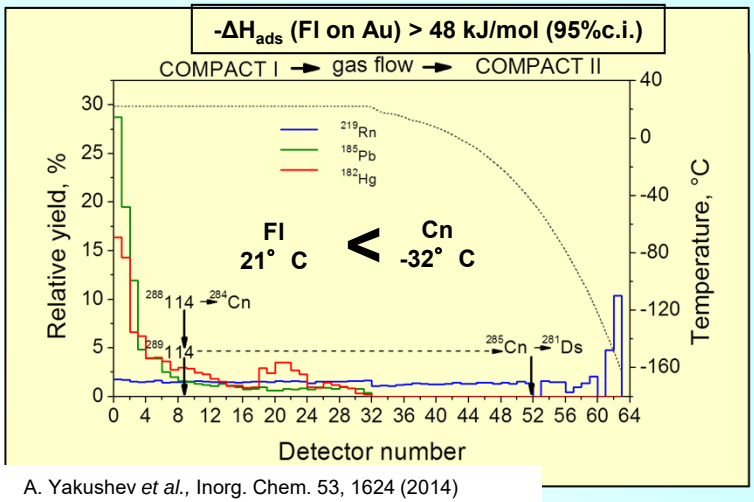
A. Yakushev: experiment on Nh and Mc, to be published

V. Pershina and M. Iliaš, 19th TASCA Workshop, May 10-12, 2022

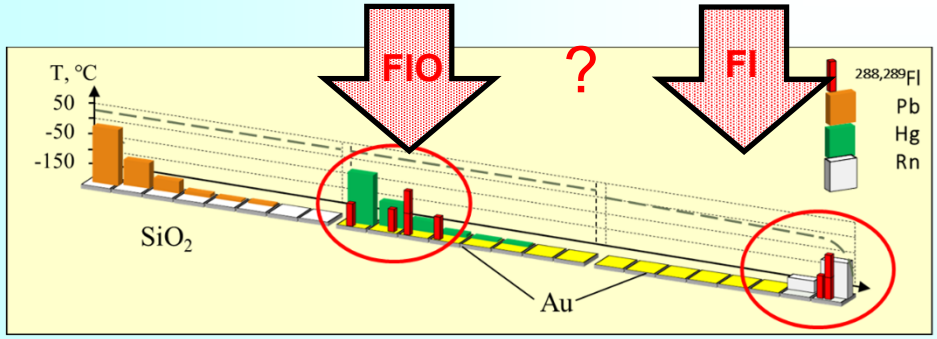
Experimental Results on Adsorption of Fl (FlO?)



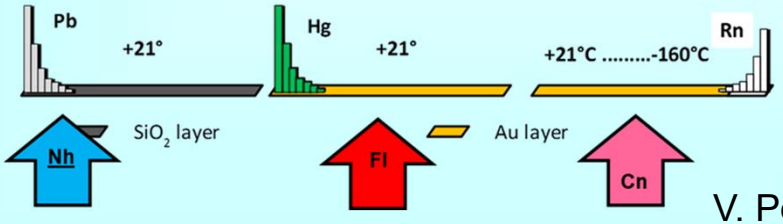
Eichler, R. *et al. Angew. Chem. Intl. Ed.* **2008**, *47*, 3262-3266.
Eichler, R. *et al. Radiochim. Acta* **2010**, *98*, 133-139.



A. Yakushev *et al.*, Inorg. Chem. 53, 1624 (2014)



A. Yakushev, *et al.*, to be submitted



Theory

$-\Delta H_{ads}^{Q}(Fl) = < 0$

$-\Delta H_{ads}^{Au}(Fl) = 68 - 89$ kJ/mol (BAND)
$= 72$ kJ/mol (VASP)

BAND:
V. Pershina, *Inorg. Chem.* **57**, 3948 (2018);
V. Pershina, M. Ilias, *Dalton Trans.* **51**, 7321 (2022)
VASP: L. Trombach et al. PCCP, **21**, 18048 (2019)

Courtesy of A. Yakushev

V. Pershina and M. Iliaš, 19th TASCA Workshop, May 10-12, 2022

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

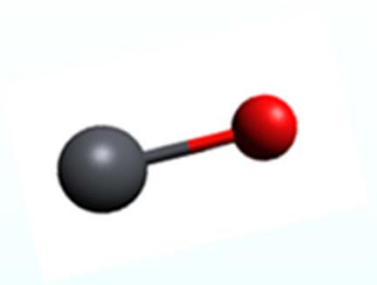
- Formation of MO, MO_2 and M(OH) in the atmosphere of O_2, H_2O and H_2
  - reaction energies
  - properties of atoms/molecules (geom., IP, α, μ)
- Predictions of adsorption properties of M, MO, M(OH) on surfaces of quartz and gold
  - structures
  - adsorption energies
  - analysis of bonding

Methods and Software – Molecular codes

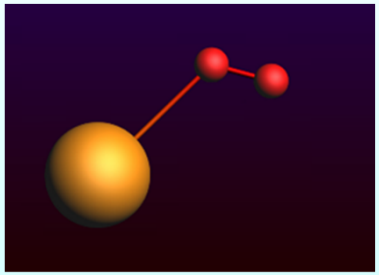
- SCM (ADF)
  - 2c-DFT; SR and SO relativity; all-electron; various E^{xc}; STO basis sets for SHEs
  - energy, properties, fast geometry optimization
  - *commercial & host-locked*
- DIRAC
  - 2c/4c-DFT + CC – *ab-initio*; all electron, Gaussian orbitals; poor geometry optimization, *free-of-charge*
- ReSpect
  - 4c-DFT, fast, Gaussian orbitals, all electron, only single points, *free-of-charge*

Formation of Oxides in the Gas-Phase (ADF Molecular Calculations)

- Hg/Cn
  - $Hg + O_2 = HgO + O$ Er = 5.322 eV
  - $Hg + O_2 = HgOO$ Er= 0.014 eV
  - $Hg + O = HgO$ Er= -0.618 eV
  - $Cn + O_2 = CnOO$ Er= 0.005 eV
  - $Cn + O = CnO$ Er= -0.733 eV



- Fl
  - $Fl + O_2 = FlO + O$ Er = 3.993 eV
  - $Fl + O_2 = FlOO$ Er = -0.044 eV
  - $Fl + O_2 = OFlO$ Er = -0.003 eV
  - $Fl + O = FlO$ Er = -1.947 eV
  - $Fl + O_3 = FlO + O_2$ Er = -0.348 eV

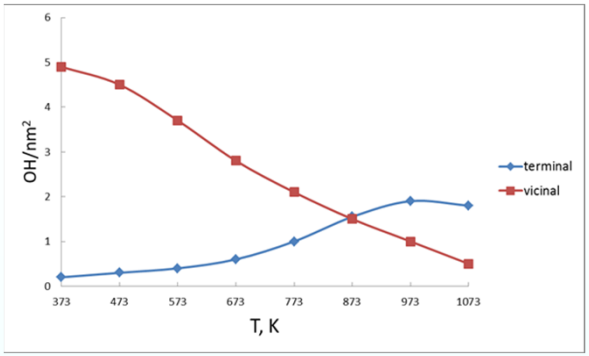


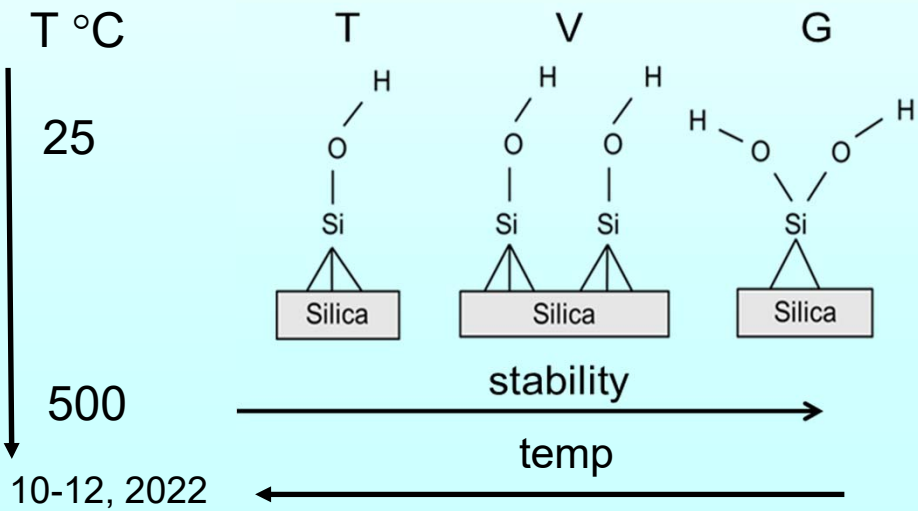
Calculations of Adsorption Properties

- Modeling (unknown) surfaces (based on data)
  - various crystals (cal-s) – most stable
  - various geometrical plane cuts – different stability
  - reconstruction of the cleaved surface (temperature)
  - modification of the crystal surface
    - temperature
    - humidity
- Applying periodic codes (BAND)
  - calculations for (chosen) systems: solid, slab, scells
  - a large number of calculations, as surfaces and adsorption positions are unknown
  - comparison with experimental E_{ads} (relative values)

Modeling Quartz Surfaces

- Crystal structure
  - α-quartz; β –crystobalite
- Surface modeling
  - planes: (001), (010), etc.
  - construction of slab, supercell (*n* layers, 4x4 unit cell)
  - crystalline or amorphous silica surface
  - surface modification
    - geminals (G) (001)
    - vicinals (V) (001) (010)
    - terminated (T)
    - hydrogen bonded (H)
    - oxygen bridged (B)





Construction of (4 x 4) Unitcells

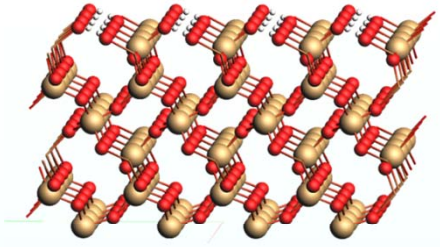
- Geminals
  - (001)

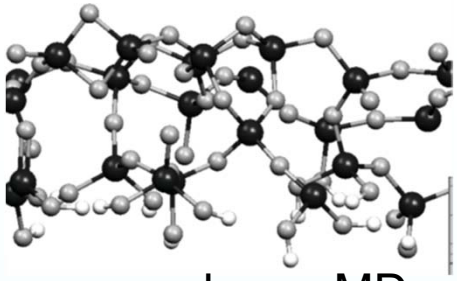
    most stable
- Vicinals
  - (001) and (010)

    → stability
- Bridged
  - (010)

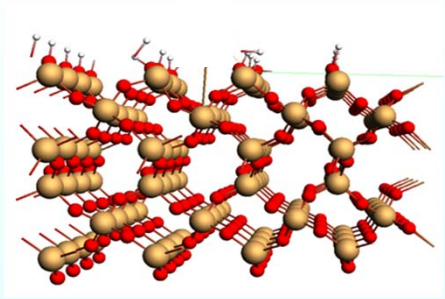
    least stable

    > 320 atoms

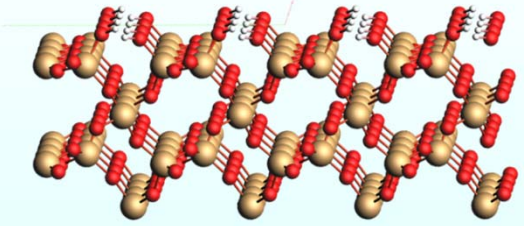


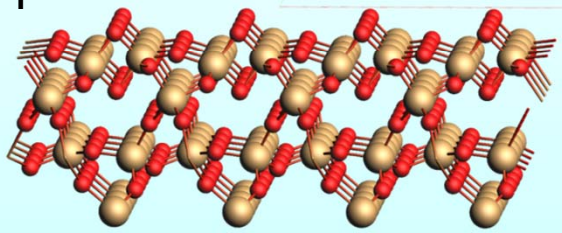


amorphous: MD



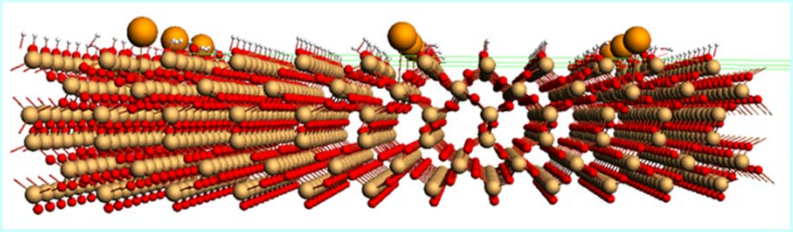
room T





> 130 °C

> 500 °C

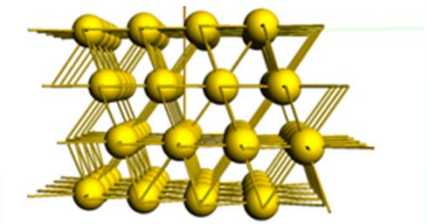


Method for Periodic Calculations

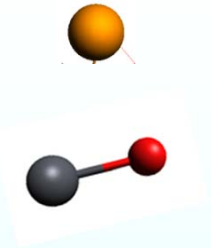
– SCM (ADF) BAND
  - 2 component: SR and SO relativity
  - all electron
  - geometry optimization (up to 300 iterations)
  - full relaxation
  - various E^{xc} (E_{ads}(Hg) and E_{ads}(Pb) on Au(111) in kJ/mol)
    – PW91 45 230 (overbinding)
    – revPBE < 0 126 (underbinding)
    – revPBE-D3BJ 78 268
    – PBE-D3 (VASP) 75 265
    – exp. 98 234 (Haenssler, 2003)
  - costly: cheking all adsorption positions
    – (for molecules: Force Field method –*extra license*)
  - *commercial & host-locked*

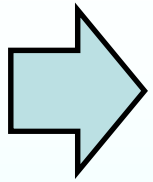
Periodic Calculations of E_{ads}(Pb/Fl) on Au(111)

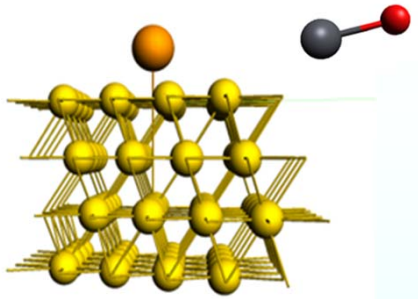
Au(111) s-cell | Atom/Molecule | M/MO/Au-s-cell



+







E_f(Au-sc)

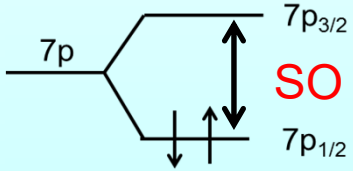
-199.5 eV

E_f (M(/MO)

Pb: -1.88 eV
Fl: -5.12 eV

E_f(M-Au$_{sc}$)

-203.8 eV
-205.1 eV



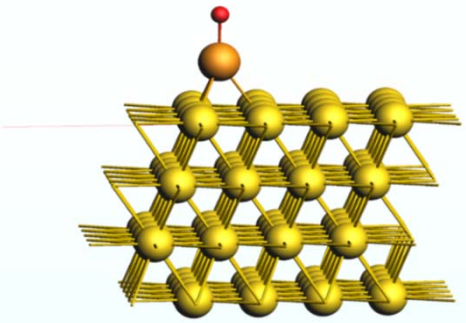
$$E_{ads} = - E_f[\text{M-Au(111)sc}] - E_f(\text{M}) - E_f[\text{Au(111)sc}]$$

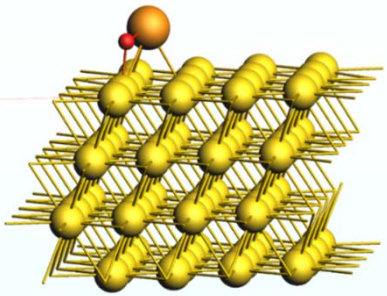
E_{ads}(M/MO) on Au(111) Surface (in eV)

HgO/CnO

PbO/FlO

s^2d^{10}



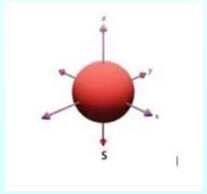


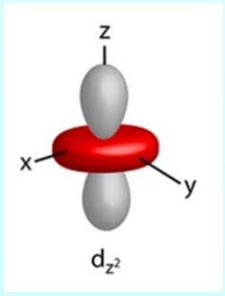
s^2p^2

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

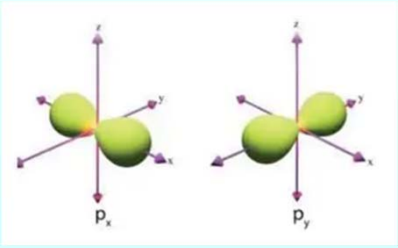
Property	Approx.	Hg	Cn	Pb	Fl
E_{ads}(M)	SR	0.79	0.60	3.80	3.76
	SO	0.81	0.62	2.79	0.92

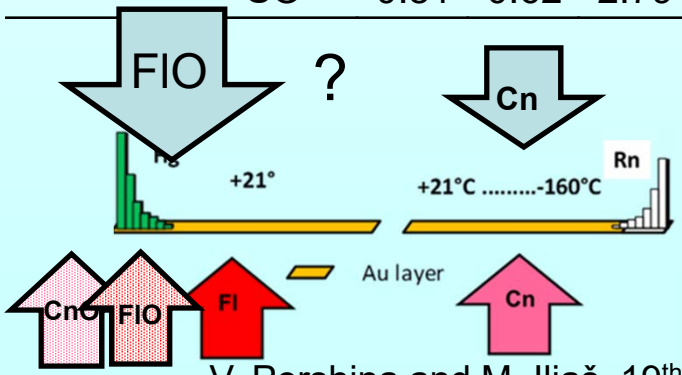
AOs





AOs



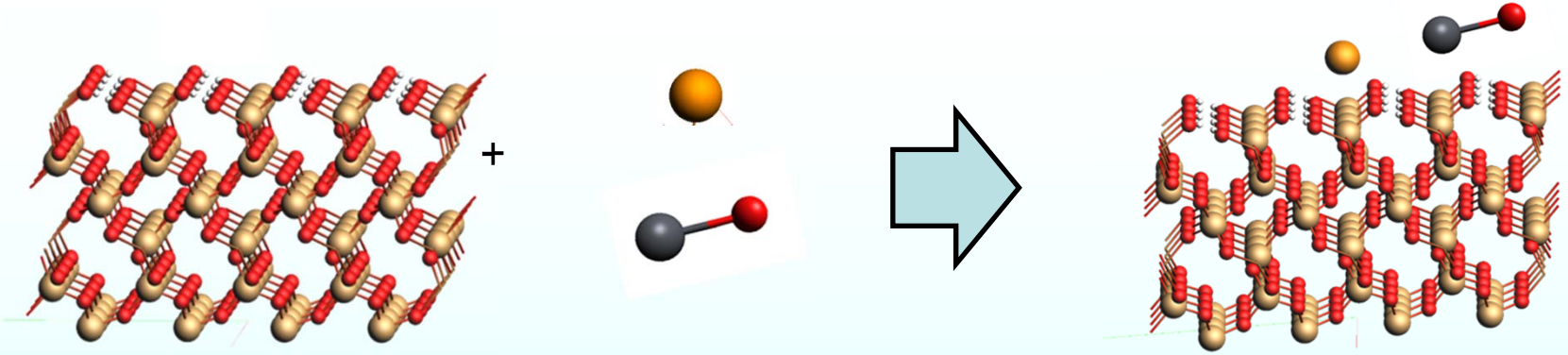


experiment

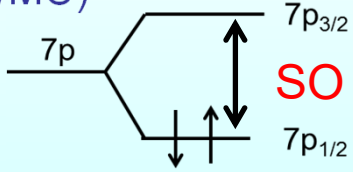
theory

Periodic Calculations of E_{ads}(M/MO) on Hydroxylated α-Quartz Surfaces (Geminals)

(001) Quartz (s-cell) Atom/Molecule M/MO/Au-s-c



$E_f(Q_{sc})$ E_f (M(/MO) $E_f(M\text{-}Q_{sc})$



Pb: -1.88 eV
Fl: -5.12 eV

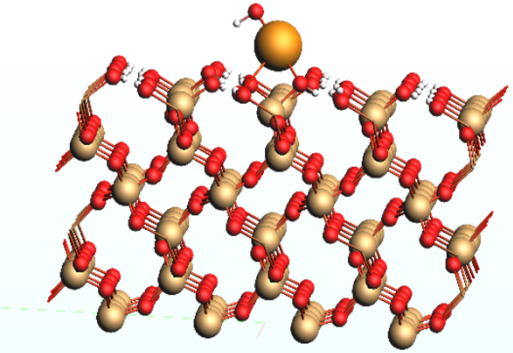
$$E_{ads} = - E_f[M\text{-}Q_{sc}] - E_f(M) - E_f[Q_{sc}]$$

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

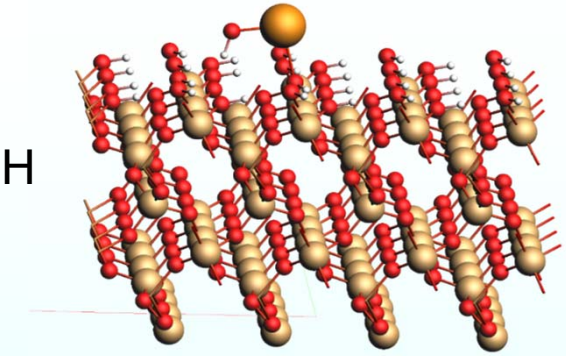
HgO/CnO

PbO/FlO

s^2d^{10}



OH-SiO_2-MOH

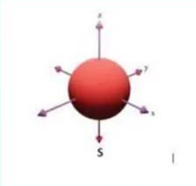


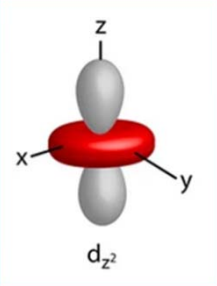
s^2p^2

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

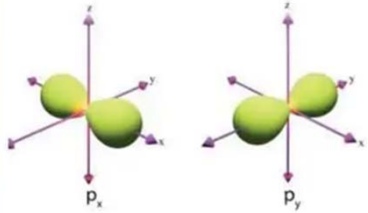
Property	Approx.	Hg	Cn	Pb	Fl
E_{ads}(M)	SR	0.28	0.29	0.72	0.15
	SO	0.28	0.29	0.22	-0.22

AOs

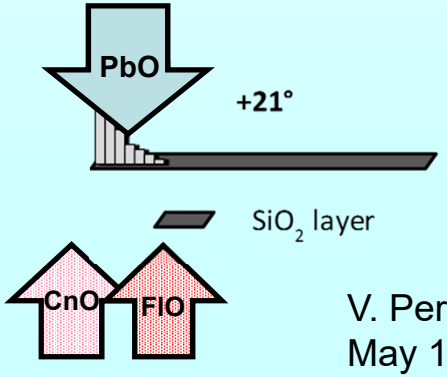




AOs



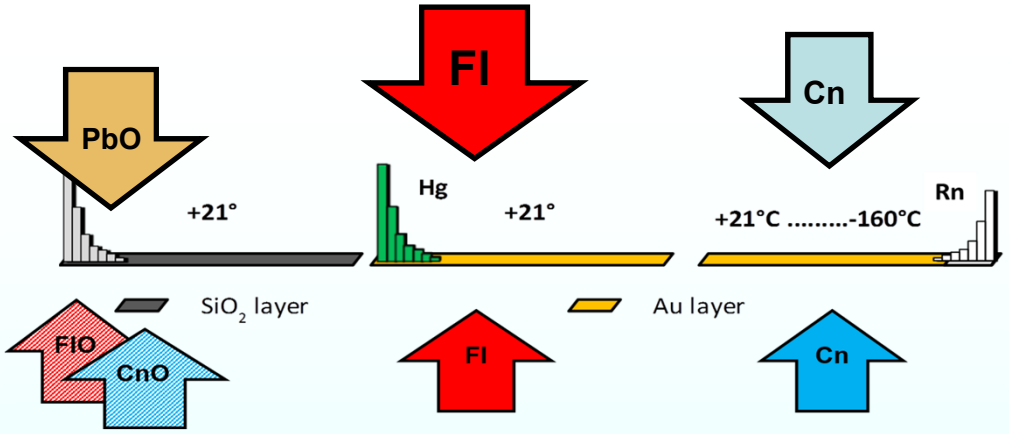
165 kJ/mol
> 67 kJ/mol



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

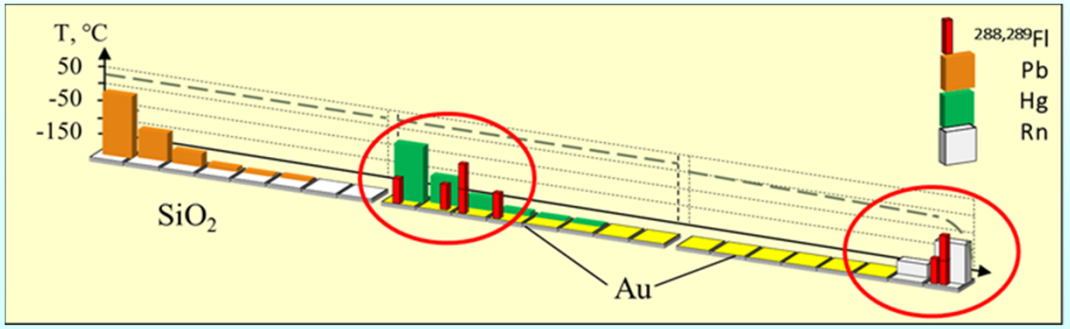
V. Pershina and M. Iliaš, 19th TASCA Workshop, May 10-12, 2022

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*., to be submitted

Thank you