Theoretical Chemistry
of Elements 112, 113 and 114

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Experiments on Adsorption of Cn, E113 and Fl on Gold and Quartz
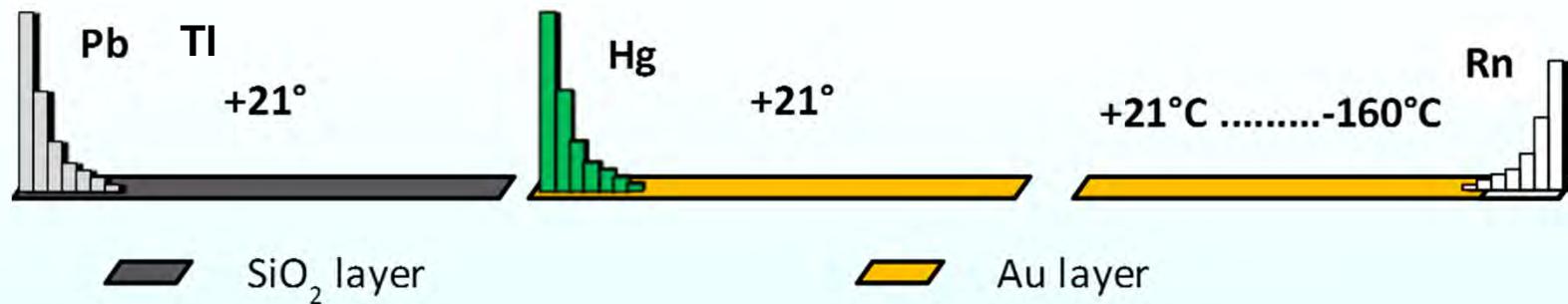


Theory: Cn, E113 and Fl ???

Experiment:

[Eichler, et al. (2007, 2010)
Yakushev, et al. (2014)]
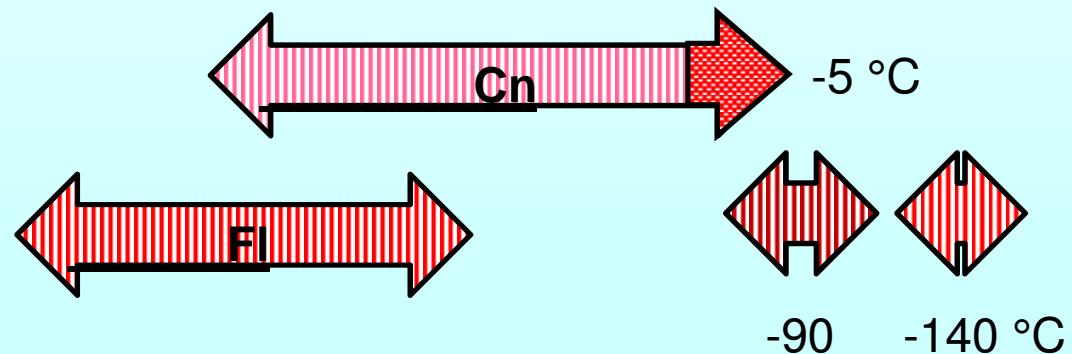
Calculations of Adsorption Energy

- Adatom-slab model (inert surface)

$$E(x) = -\frac{3}{16}\left(\frac{\varepsilon-1}{\varepsilon+2}\right)\frac{\alpha_{mol}}{\left(\dfrac{1}{IP_{slab}} + \dfrac{1}{IP_{mol}}\right)x^3}$$
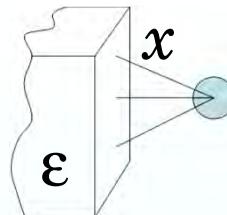
- Cluster model
  (molecular codes,
  convergence with the cluster size)

- Periodic calculations
 (slabs, supercells,
 periodic boundary conditions)
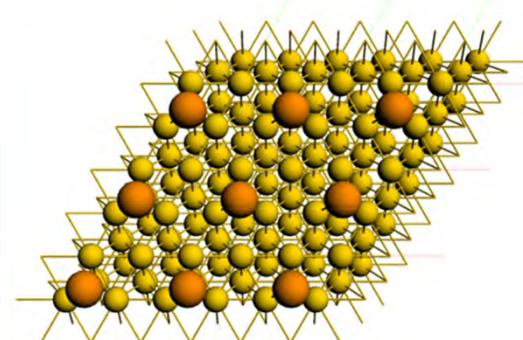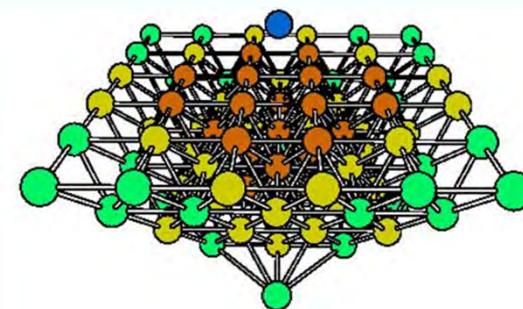
Periodic Codes

- Available (2c-/4c-DFT)
  - CASTEP (homologs)
  - WASP (PP, homologs)
  - RFPLO (Cn)
  - ADF BAND (SHE)

- ADF BAND
  - 2c-ZORA
  - SR, SO iteratively
  - basis sets till Z=120
  - TZP, TZ2P
  - all electron, frosen core
  - revPBE (no dispersive for SHE)
  - full relaxation

Adsorption of Cn, E113 and Fl on Gold

M-Au$_n$ binding energies
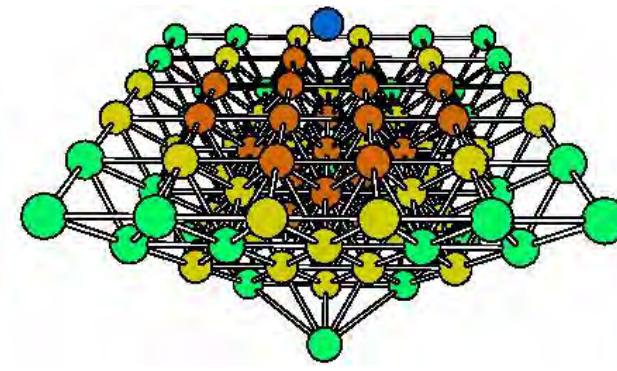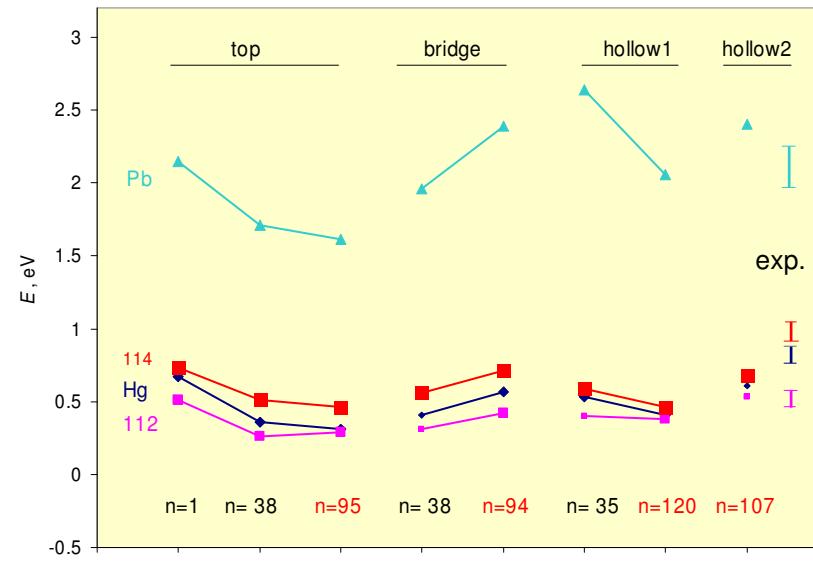
| M	position, n	E_b, eV	ΔH_{ads}, eV	Ref. (exp.)
Hg	bridge n=94	**0.56**	**0.92**	Eichler
Cn	hollow n=107	**0.46**	**0.54$^{+0.4}_{-0.03}$**	Eichler
Pb	bridge n=94	**2.40**	**2.43**	Haennsler
114	bridge n=94	**0.71**	**0.36$^{+0.5}_{-0.1}$**	Eichler
			≥ 0.5	Yakushev
Tl	bridge n=16	**2.65**	**2.48**	Serov
113	bridge n=16	**1.34**	**(1.65)**	-
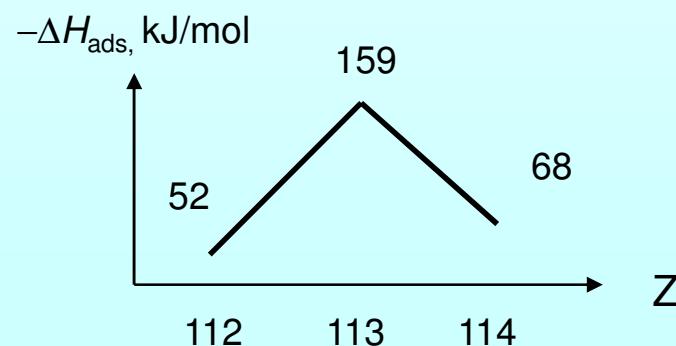
→ like HOAO

[Pershina, Anton, Jacob, JCP, 2009]

# Predictions of Adsorption of Cn, E113 and Fl on Gold and Quartz

Hydroxylated Quartz (Silanols)

stability
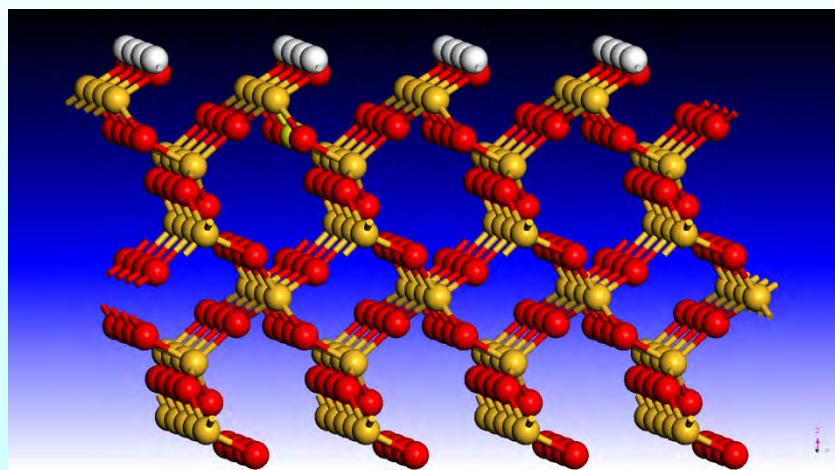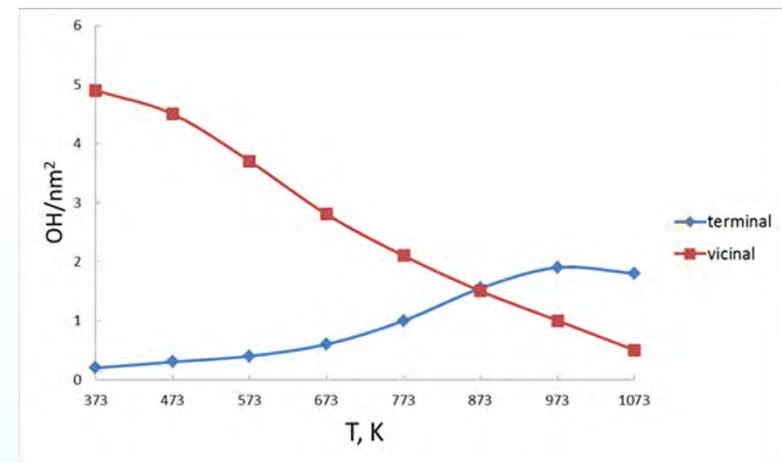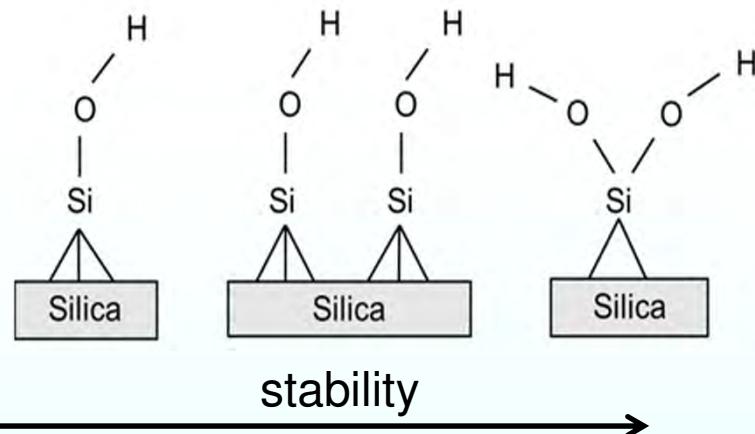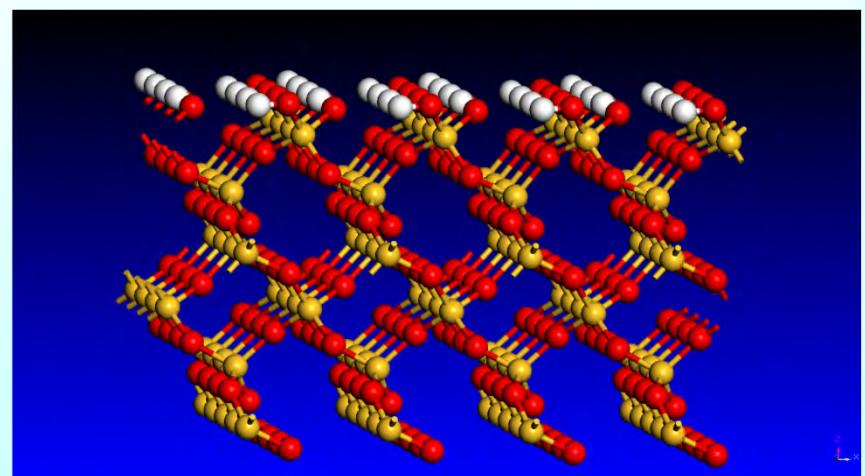
25 °C: vicinal (80%)   geminal (10%)

Influence of Coverage on E_{ads} of Pb

full (slab)
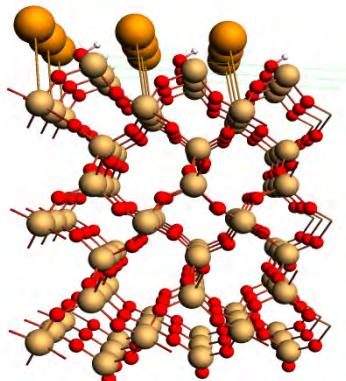
(2 x 2) supercell

1.28 eV (d = 1.48 Å)
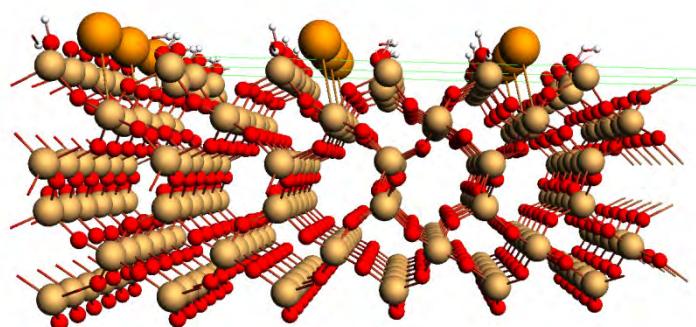
2.31 eV (d = 1.07 Å)

Exp:
2.12 eV

(4 x 4) supercell
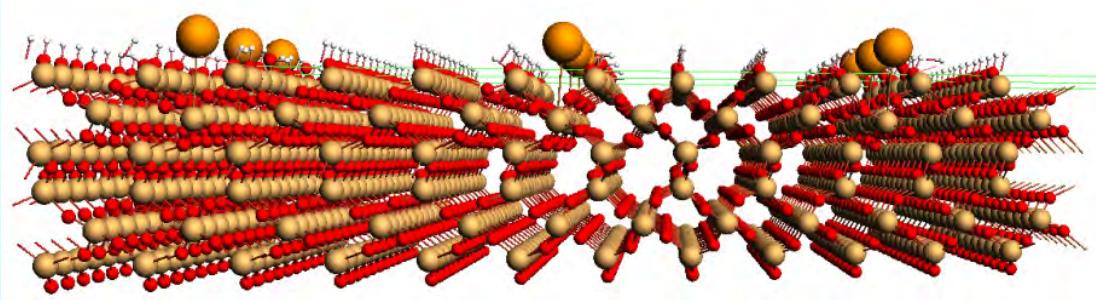
(a uni cell: > 300 atoms)   1.58 eV (d = 1.16 Å)

[V.Pershina, PCCP, 18, 17750 (2016)]

Exp:
1.66 ± 0.1 eV

Adsorption of Pb/Fl on Hydroxylated Quartz: Influence of SO Effects

E_f(SO):   2107.4   Pb: -1.87   Pb: -2110.0
                            Fl: -5.08   Fl: -2112.3

7p → 7p$_{3/2}$, 7p$_{1/2}$
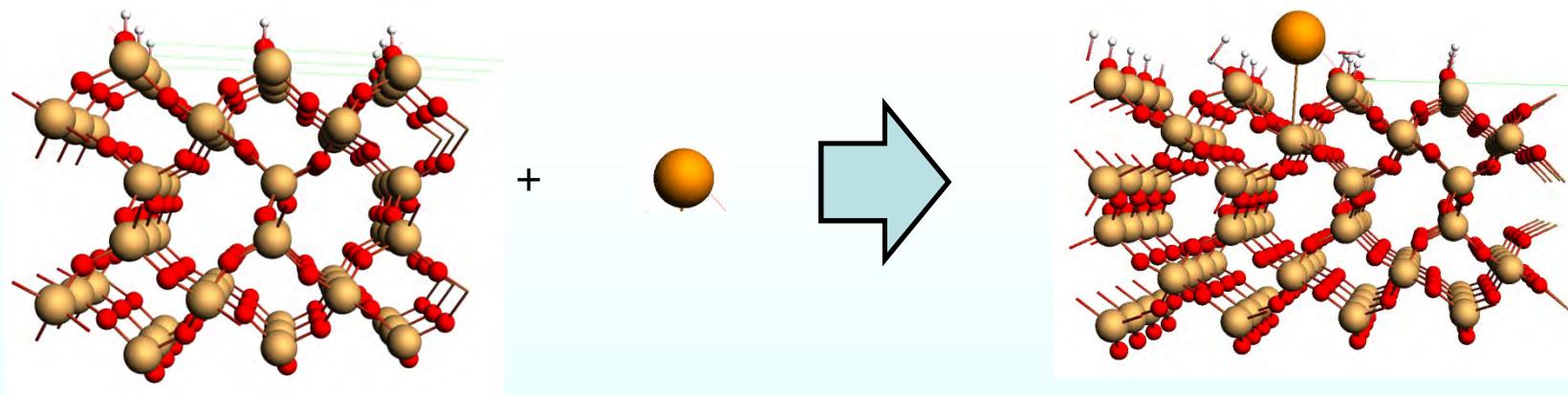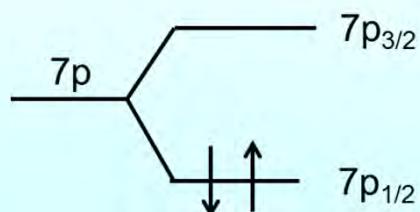
$-\Delta H_{ads}$(Pb) = 3.79 eV (SR) = 1.57 eV (SO) (exp. 1.66 eV)

$-\Delta H_{ads}$(Fl) = 3.86 eV (SR) = -0.23 eV (SO)

[V.Pershina, PCCP, 18, 17750 (2016)]

Adsorption of Group 12, 13 and 14 Elements on Quartz and Gold (-ΔH_{ads}, kJ/mol)

Surf.	Hg	Cn	Tl	E113	Pb	Fl	Method
SiO$_2$	54	-38	152	58	152	-22	ADF BAND
	42 ± 2	-	158 ± 3	-	165 ± 4	-	Exp.
Au	54	45	(240)	159 ± 15	232	68	4c-DFT
	98 ± 3	52$^{+4}_{-3}$	240 ± 5	-	234	34$^{+54}_{-11}$	Exp. Eichler
						≥ 48	Exp. Yakushev

Adsorption Energy on Gold (111)

regular Au(111) surface

Adsorption of Group-12, 13 and 14 Elements on Quartz and Gold