有機分子エレクトロニクス：界面電気二重層の解明と制御

森川良忠

大阪大学 大学院工学研究科

OSAKA UNIVERSITY

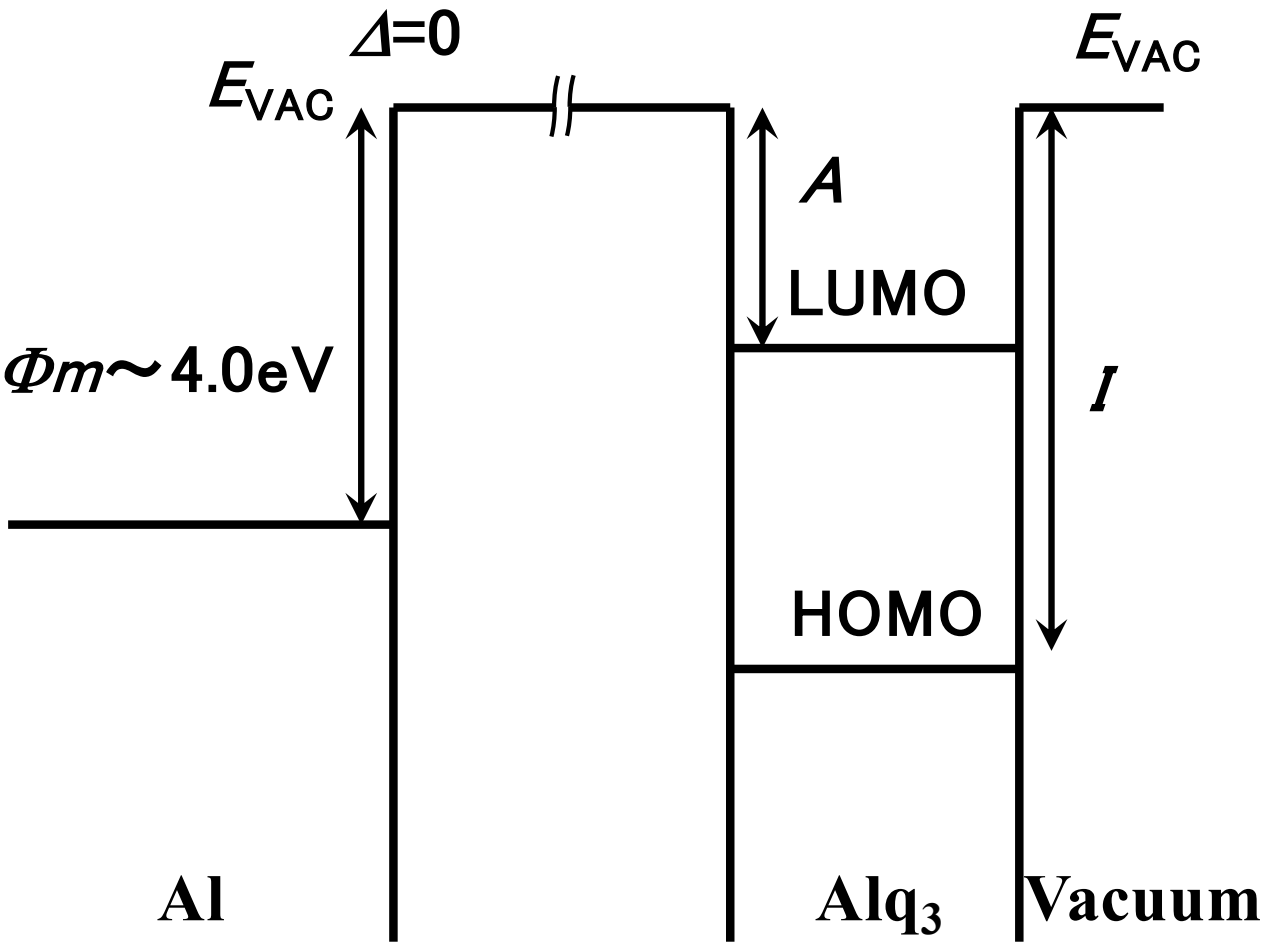
Outline

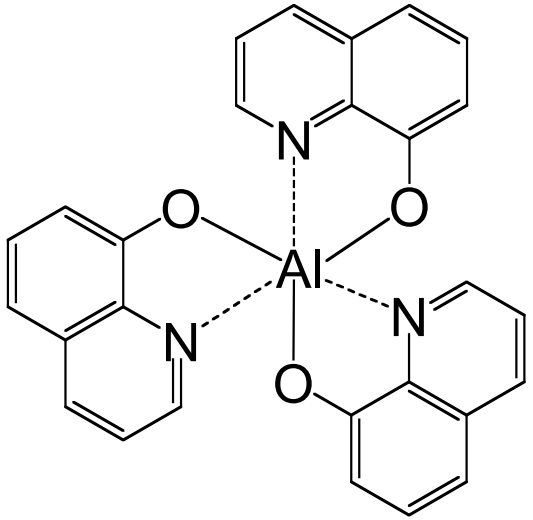
1) イントロダクション
2) *n*-アルカン: 典型的な物理吸着系
   関一彦(名古屋大学), 石井久夫(千葉大学)、
   Kyuho Lee(Rutgers Univ.)
3) ベンゼン, ペンタセン/貴金属界面：芳香族炭化水素
   豊田健治, 柳澤将 (大阪大学, パナソニック),
   濱田幾太郎(東北大学),
   Kyuho Lee (Rutgers Univ.)
4) Alq_3/金属界面: 有機EL材料
   柳澤将(大阪大学)
   Kyuho Lee (Rutgers Univ.)
5) 今後の課題

有機/金属界面

- Organic devices such as organic electroluminescent devices (OEL), organic field effect transistors (OFET), and organic photovoltaic cells are attracting enormous attention.
- Metal/Organic interfaces play important roles in determining the efficiency of organic devices.

Interfacial Dipole Layer





Alq3: tris-(8-hydroxy quinolinato) aluminum
Most widely used electron-transport material in organic light emitting device.

H. Ishii, K. Sugiyama, E. Ito, and K. Seki, *Adv. Mater.*, 11, 605 (1999).

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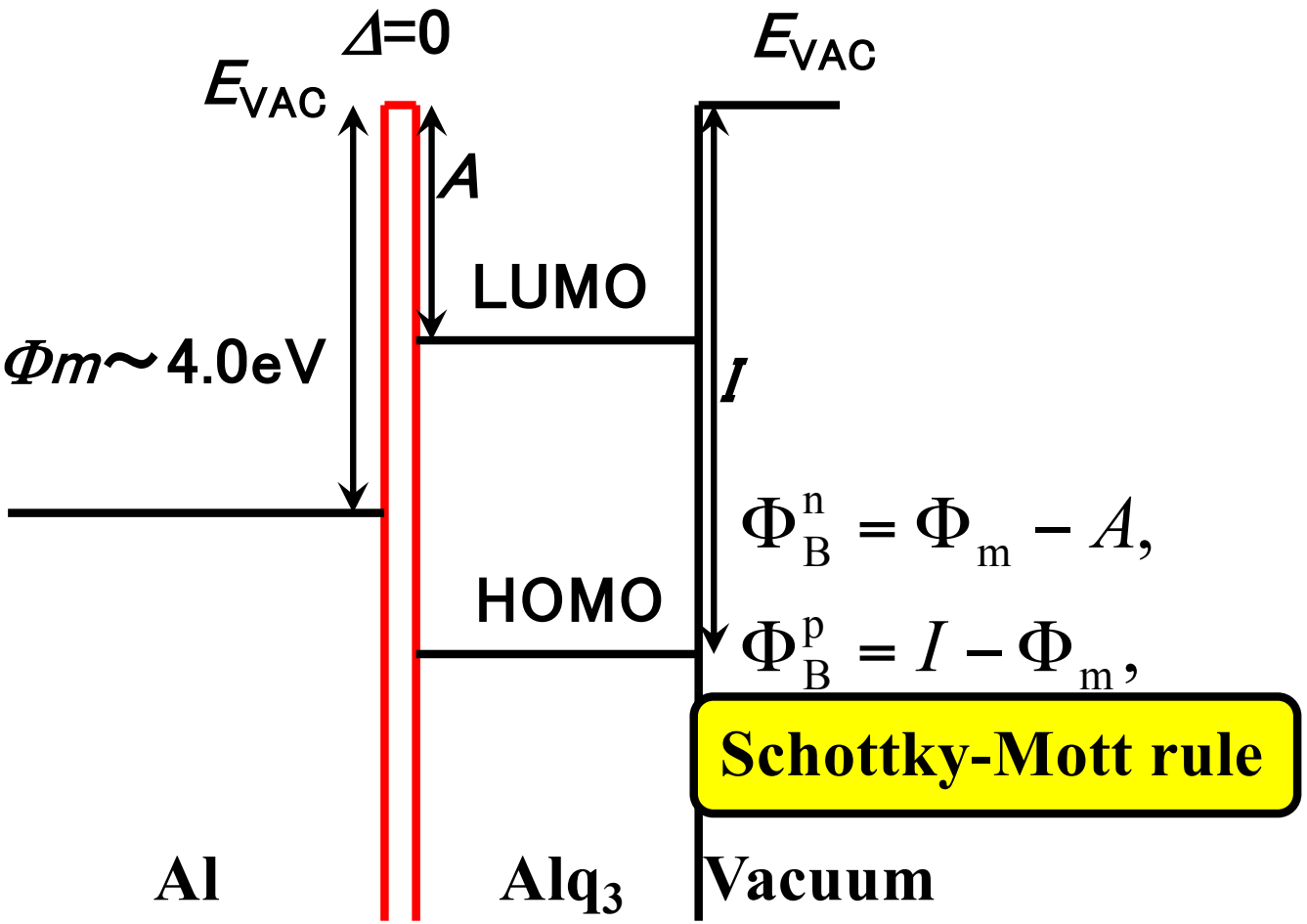

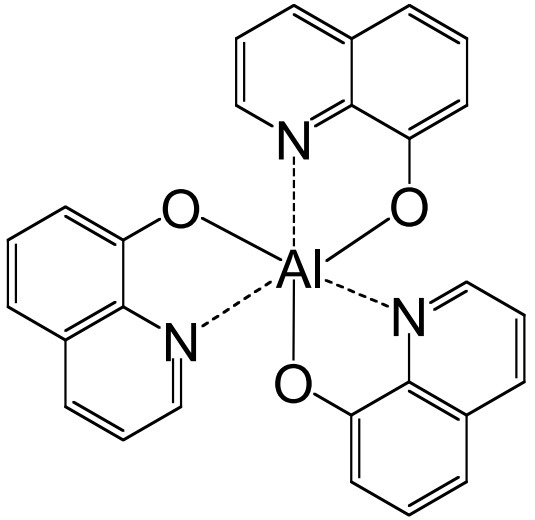

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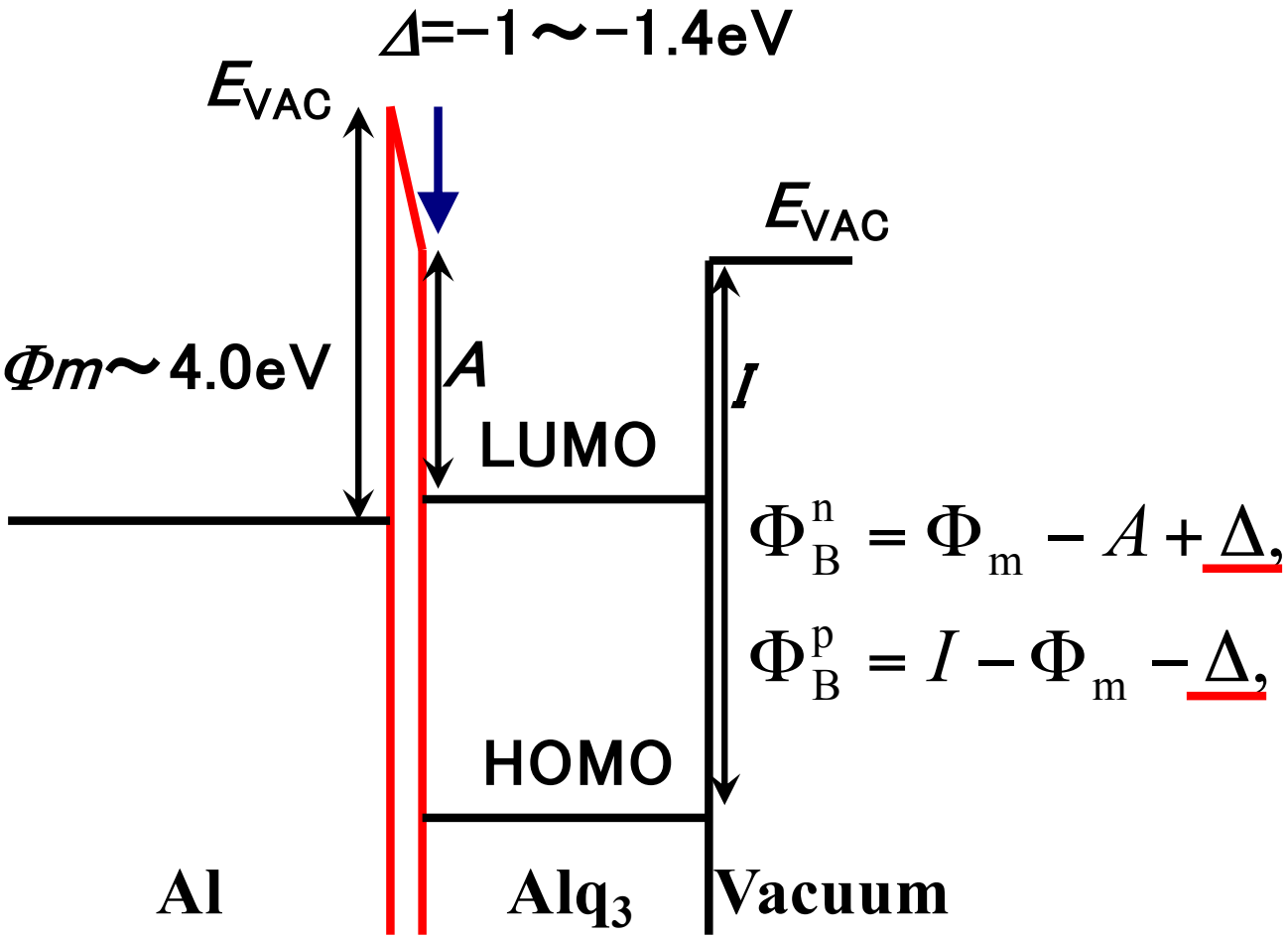

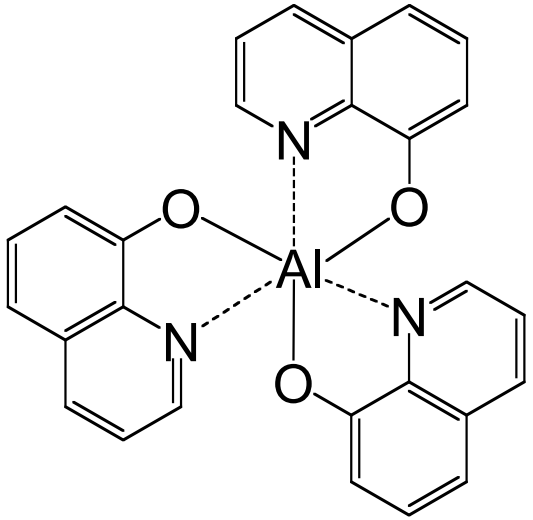

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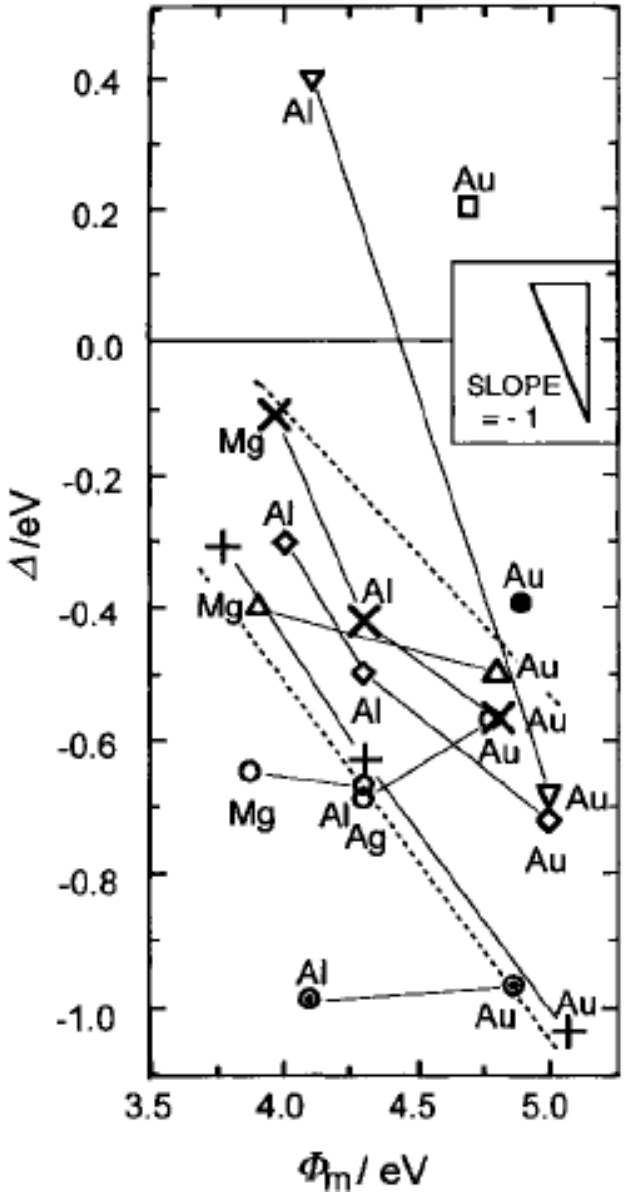
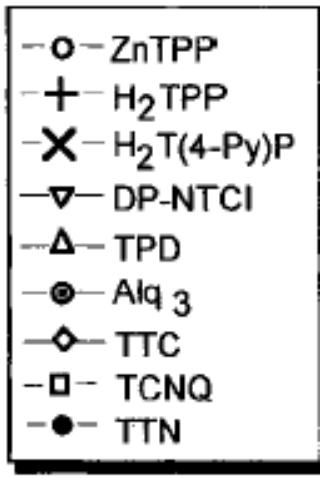
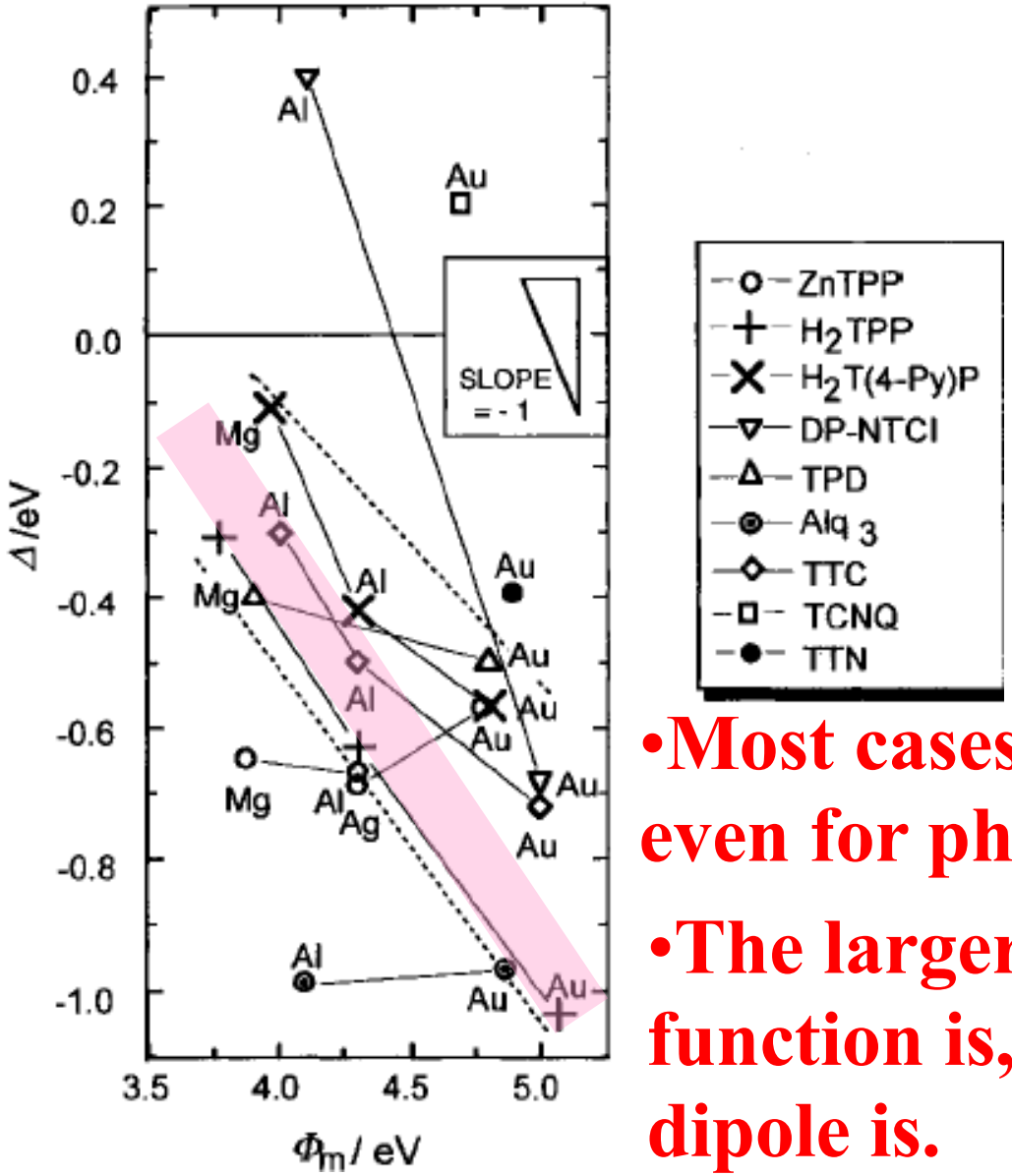
Substrate and Molecular Dependence





- **Most cases, work function is reduced even for physisorbed systems.**

Substrate and Molecular Dependence



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- **The larger the substrate work function is, the larger the interface dipole is.**

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Interface Slope Parameter

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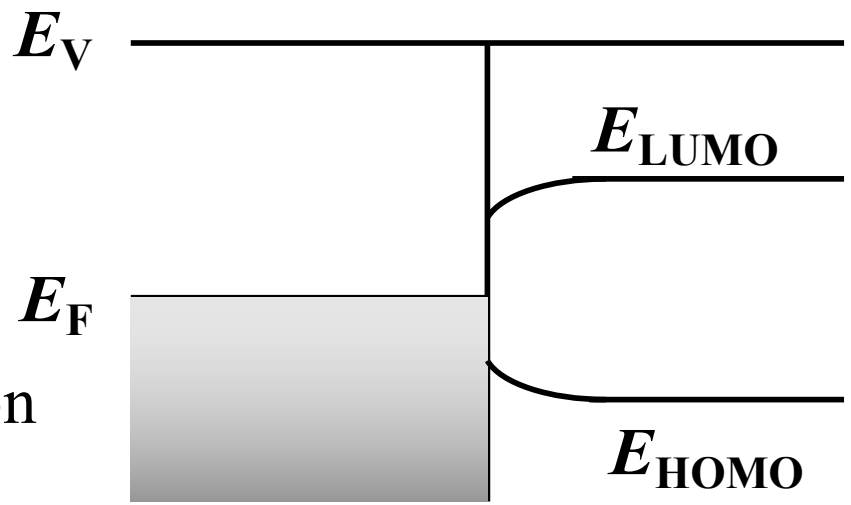

Schottky Limit. Weak Interaction

$$S = 1 \Leftrightarrow \frac{d\Delta}{d\Phi_m} = 0$$

Bardeen Limit Fermi Level Pining

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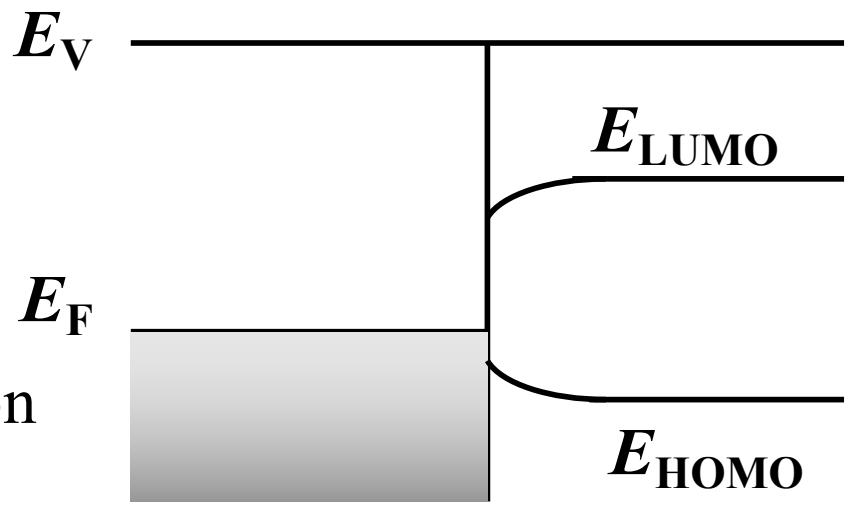

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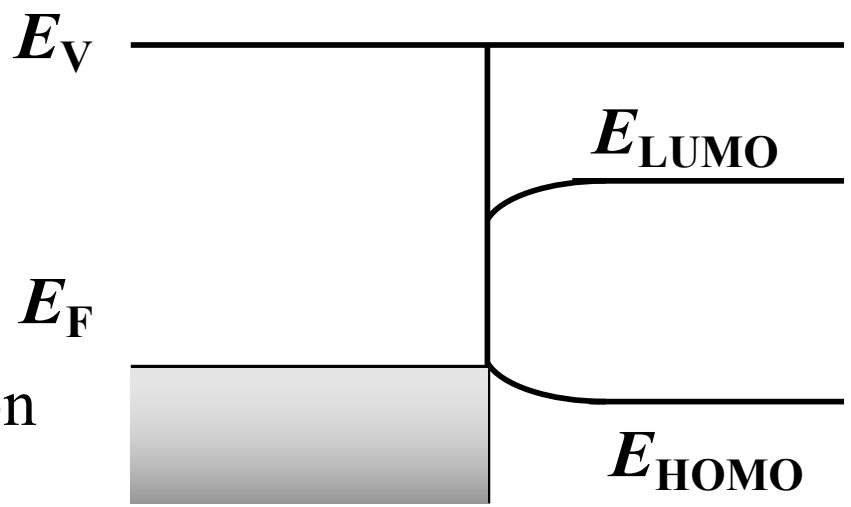

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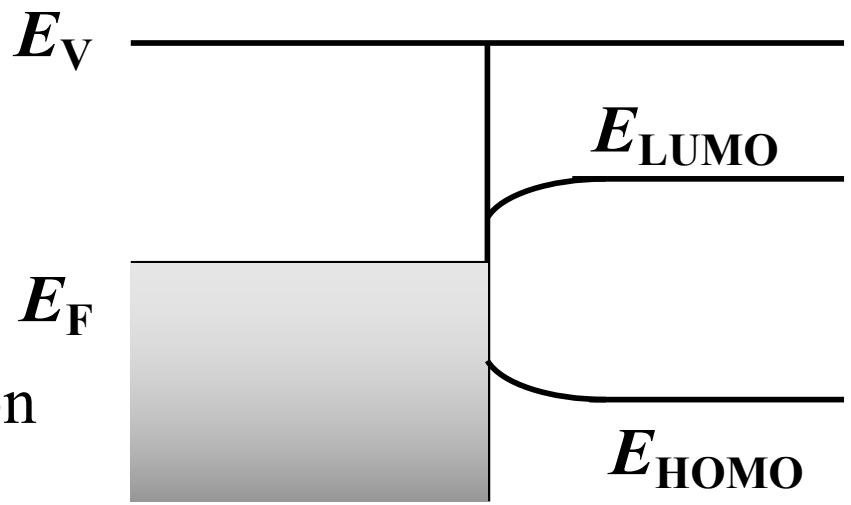

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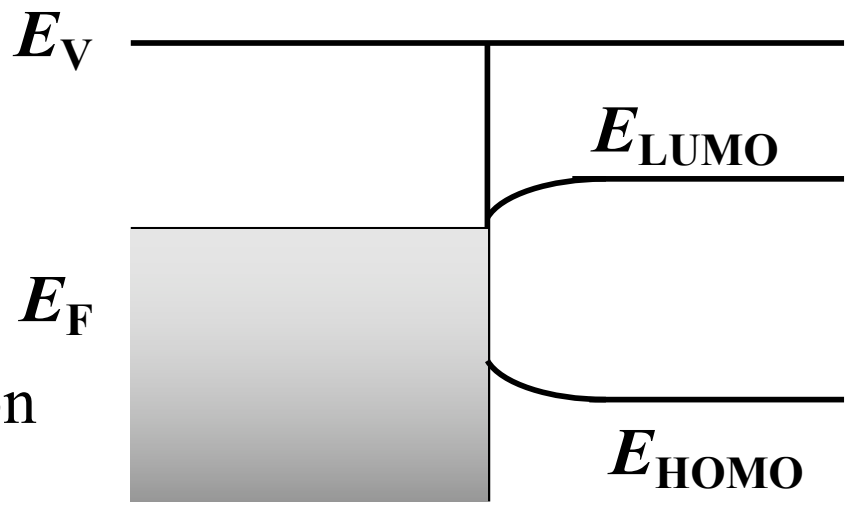

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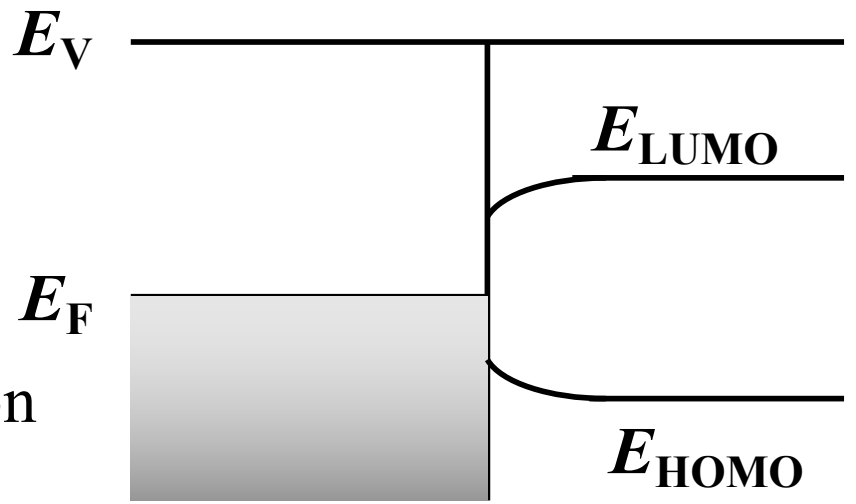

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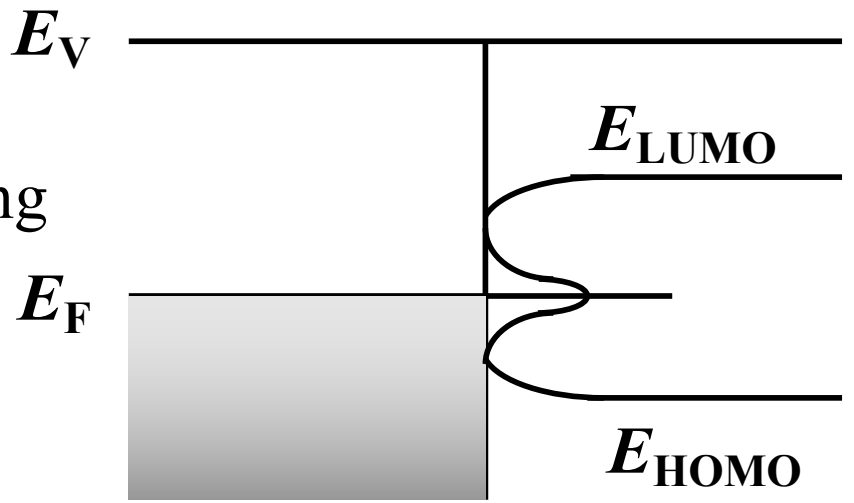

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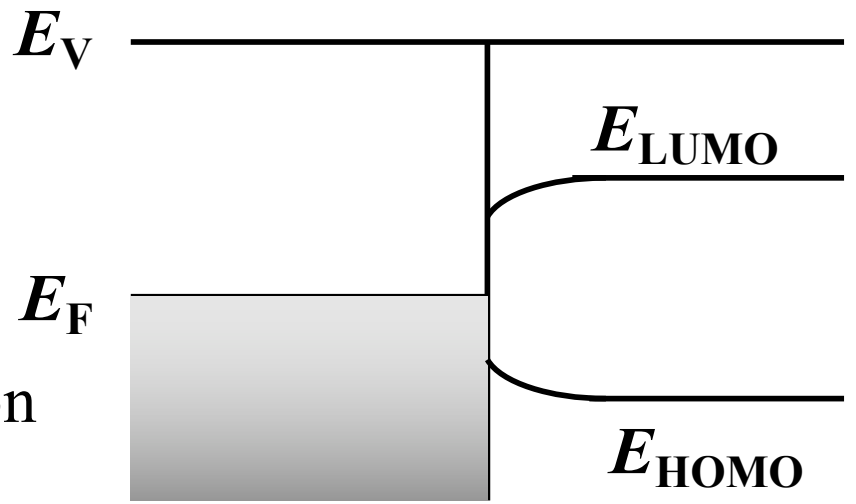

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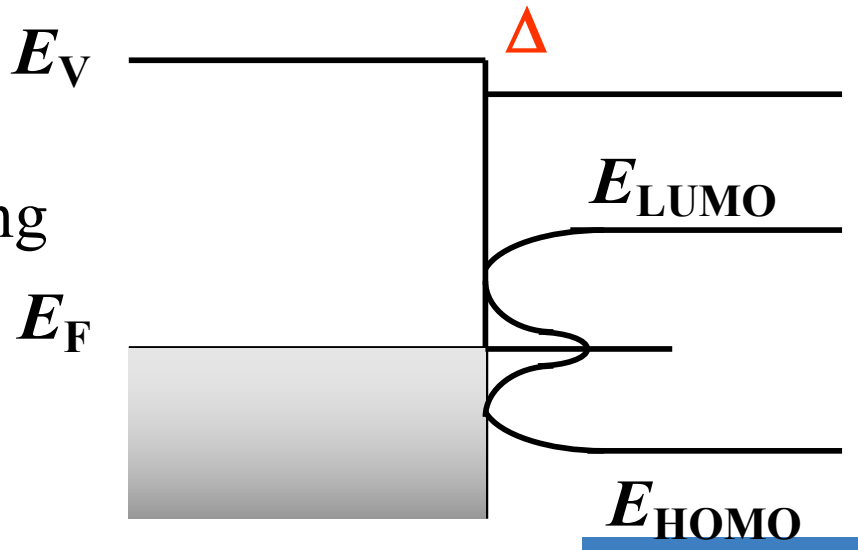

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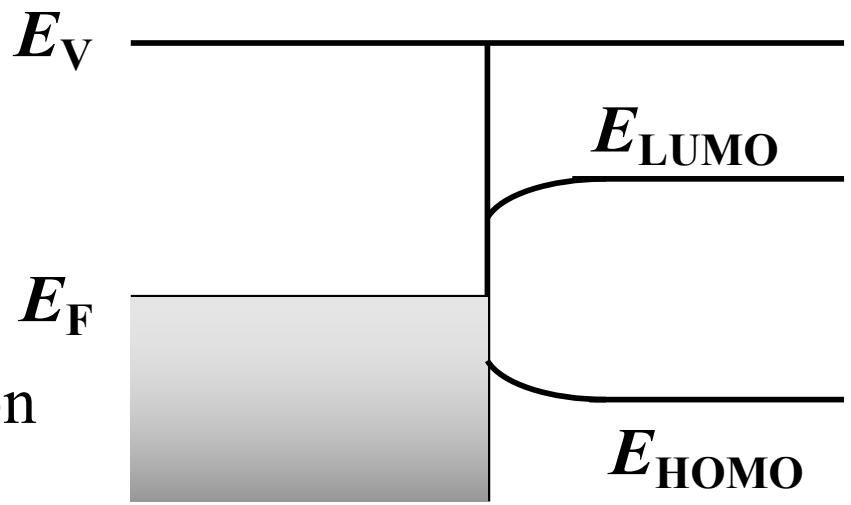

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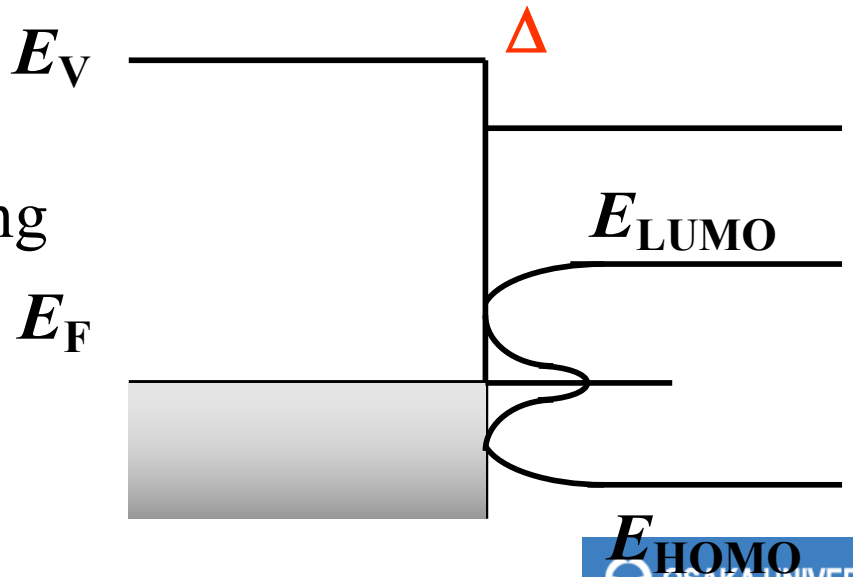

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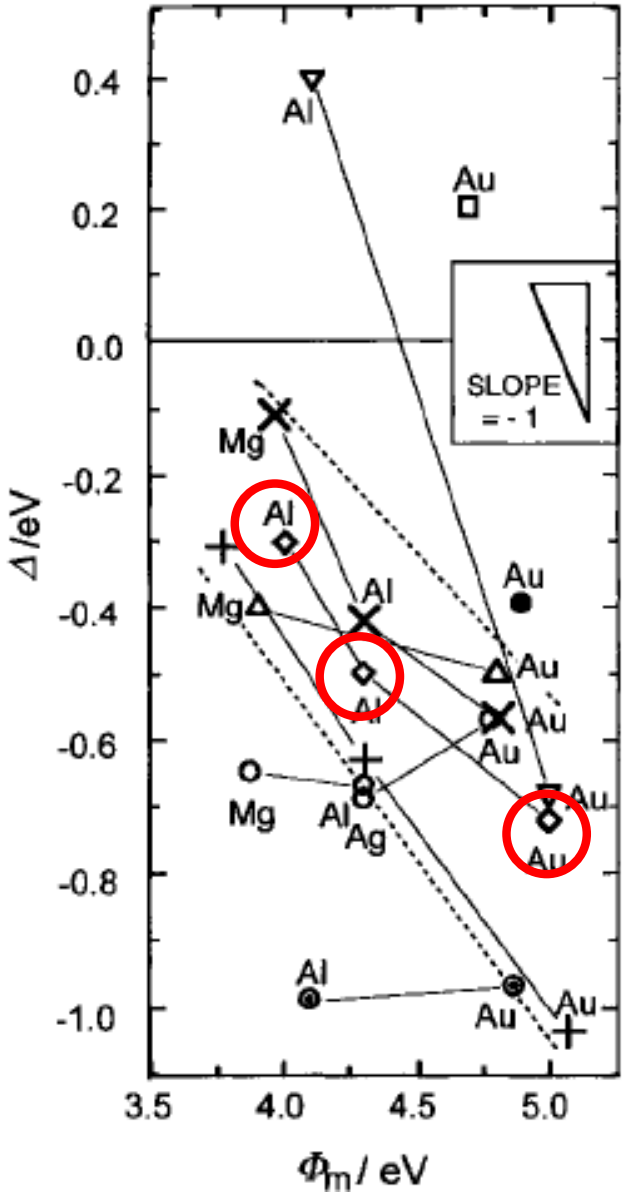

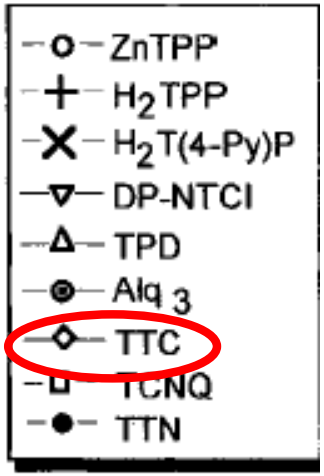

この画像は表示できません。

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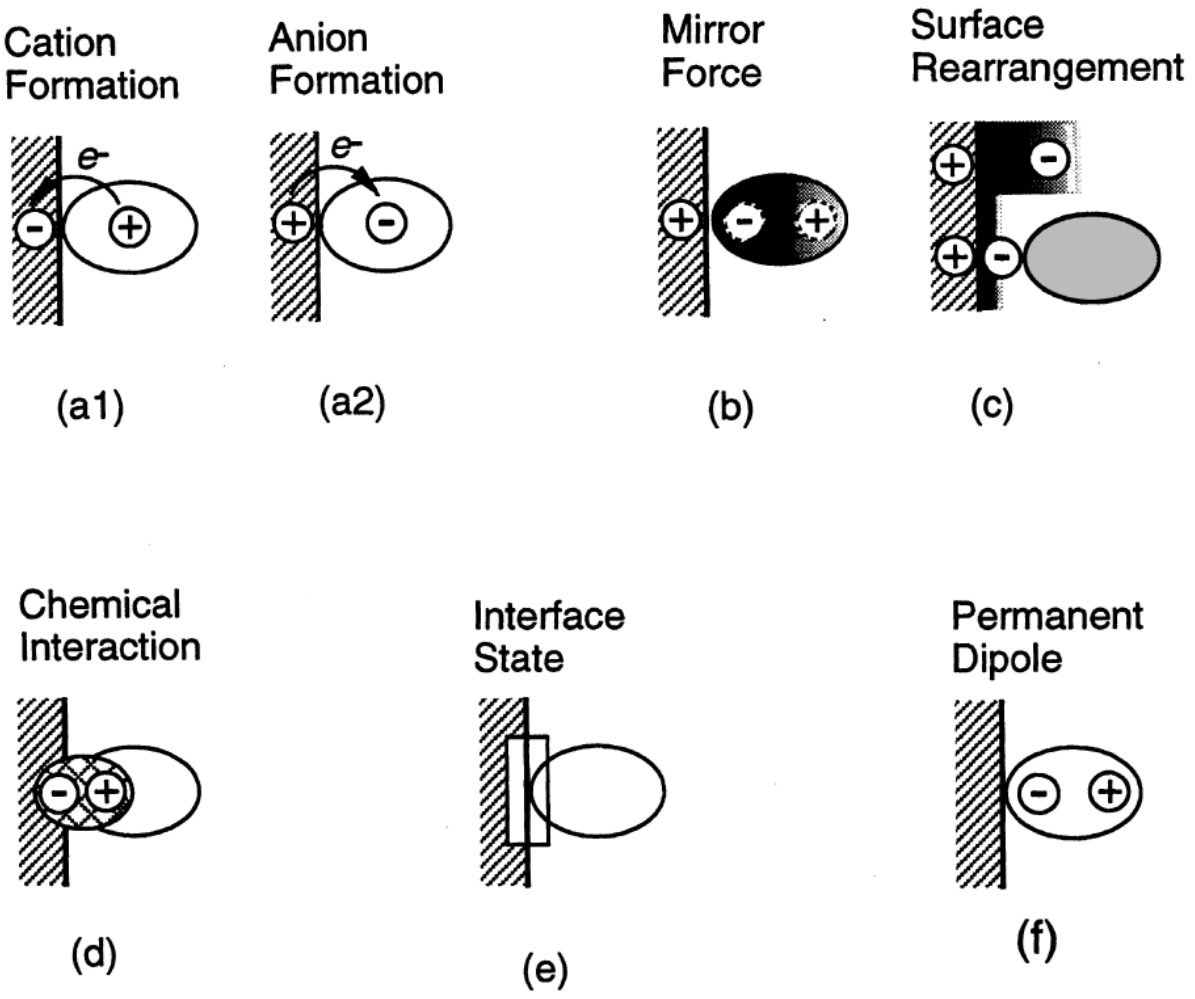
Origins of Interfacial Dipole Layer

Charge Transfer

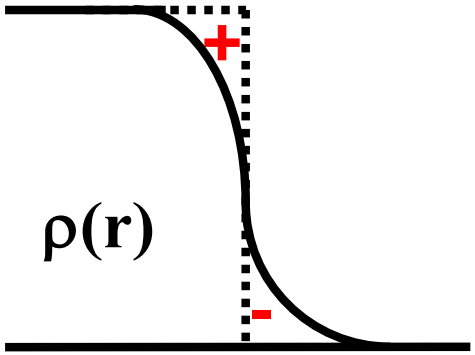


Origin of the Substrate Dependence

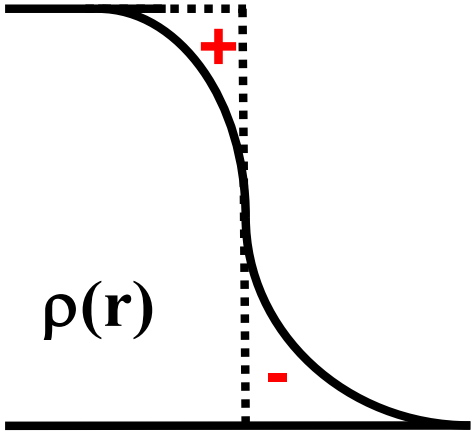
Larger Substrate Work Function

→Larger Surface Dipole Layer Formed by a Larger Penetration of Electrons into Vacuum

→ Larger Push-Back Effect by Molecules.



Φ small **small penetration**



Φ large **Large penetration**

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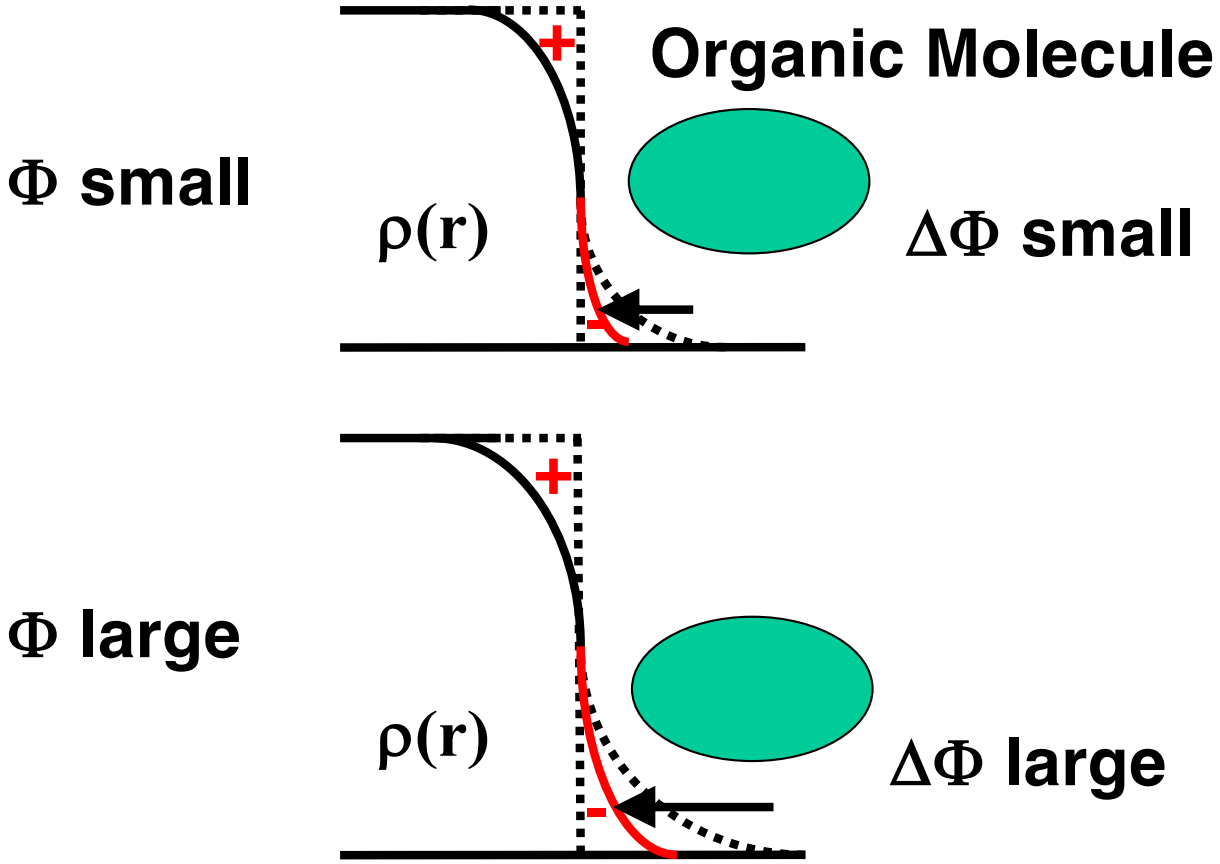


DFT Calculations

- Ab Initio Code “STATE-Senri”
- (Simulation Tool for Atom TEchnology)
- DFT-GGA (PBE96)
- Long-range van der Waals interaction is included by

  1) Semi-empirical DFT-D:

  S. Grimme, J. Comput. Chem. 27, 1787 (2006).

  2) Ab initio vdW-DF:

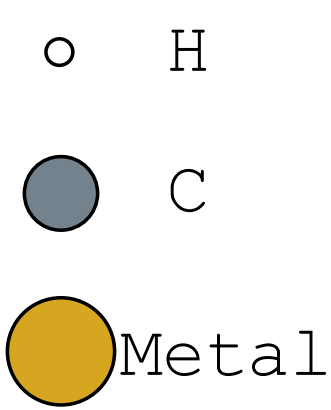
  M. Dion et al., Phys. Rev. Lett., 92, 246401 (2004).

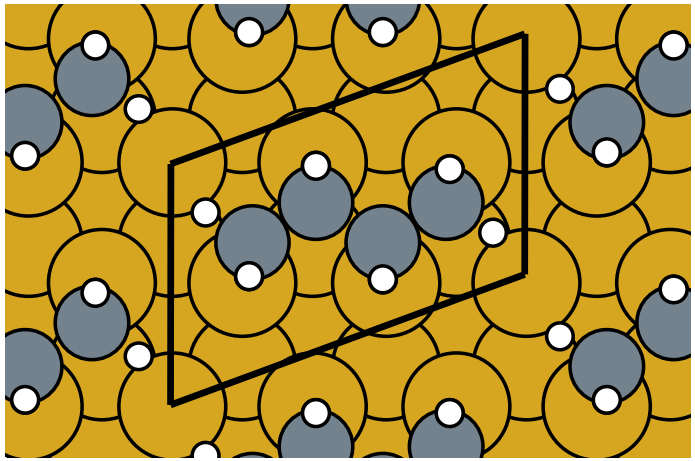
Workfunction

Metal	DFT (eV)	Exp.
Mg(001)	3.72	3.66*
Al(111)	4.09	4.24
Cu(100)	4.51	4.59
Cu(111)	4.58	4.98
Ru(001)	5.03	4.71*
Ag(111)	4.46	4.74
Pt(111)	5.76	5.93
Au(111)	5.15	5.31

* Polycrystal

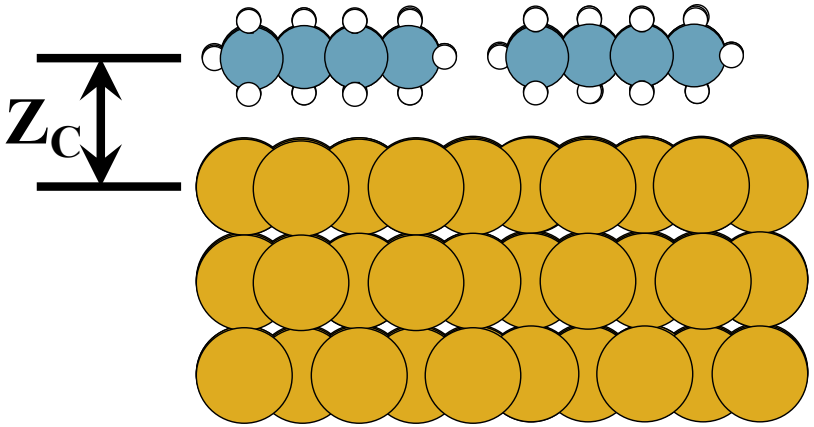
Butane on Pt(111)





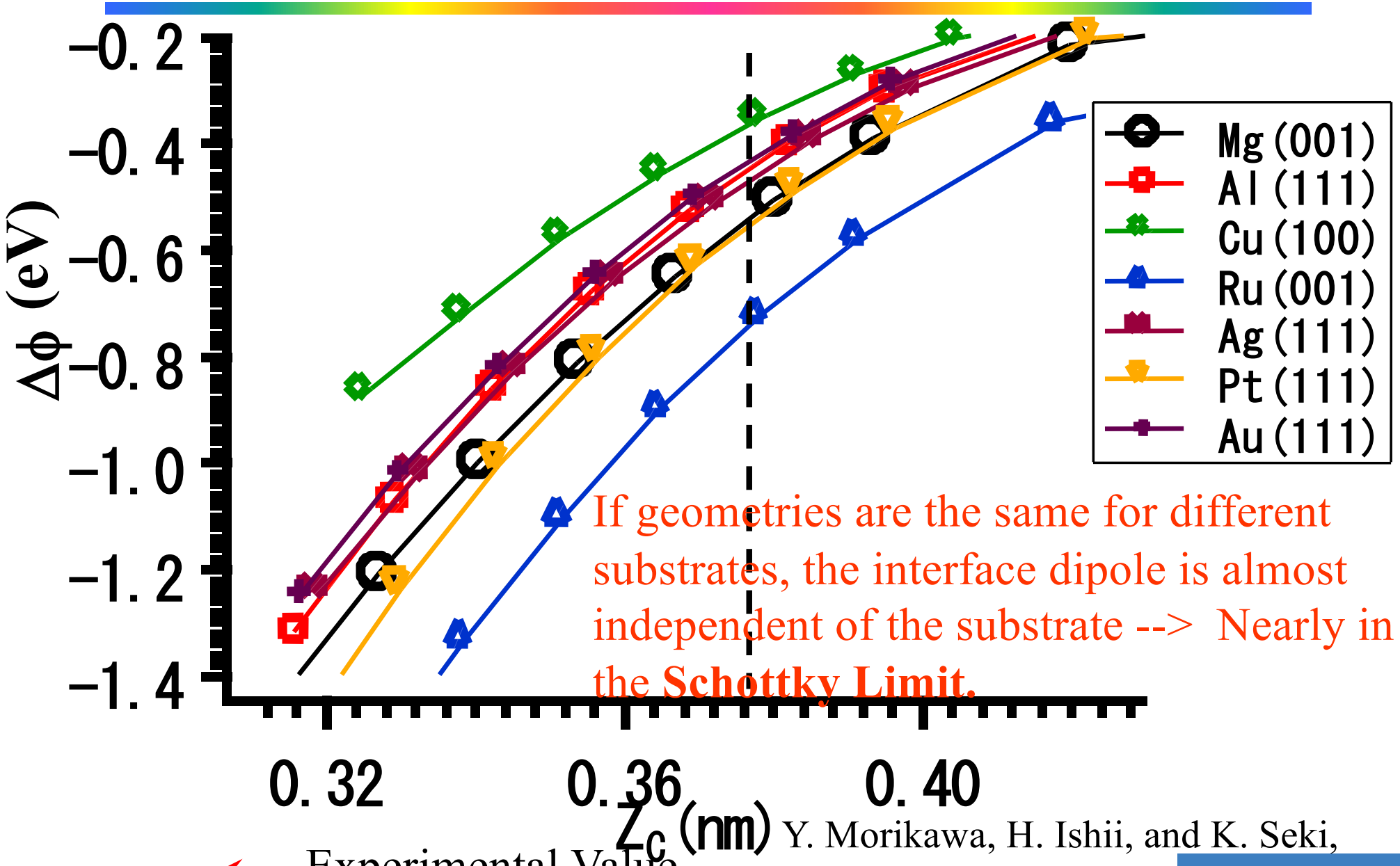
L.E.Firment and G.A. Somorjai,
J. Chem. Phys., **66**, 2901 (1977).

$$\begin{vmatrix} 2 & 1 \\ \bar{1} & 2 \end{vmatrix}$$



We adopted this structure also for Mg(001), Al(111), Cu(111), Ru(001), Ag(111), and Au(111) surfaces.

Workfunction Change: n-alkane on Metals



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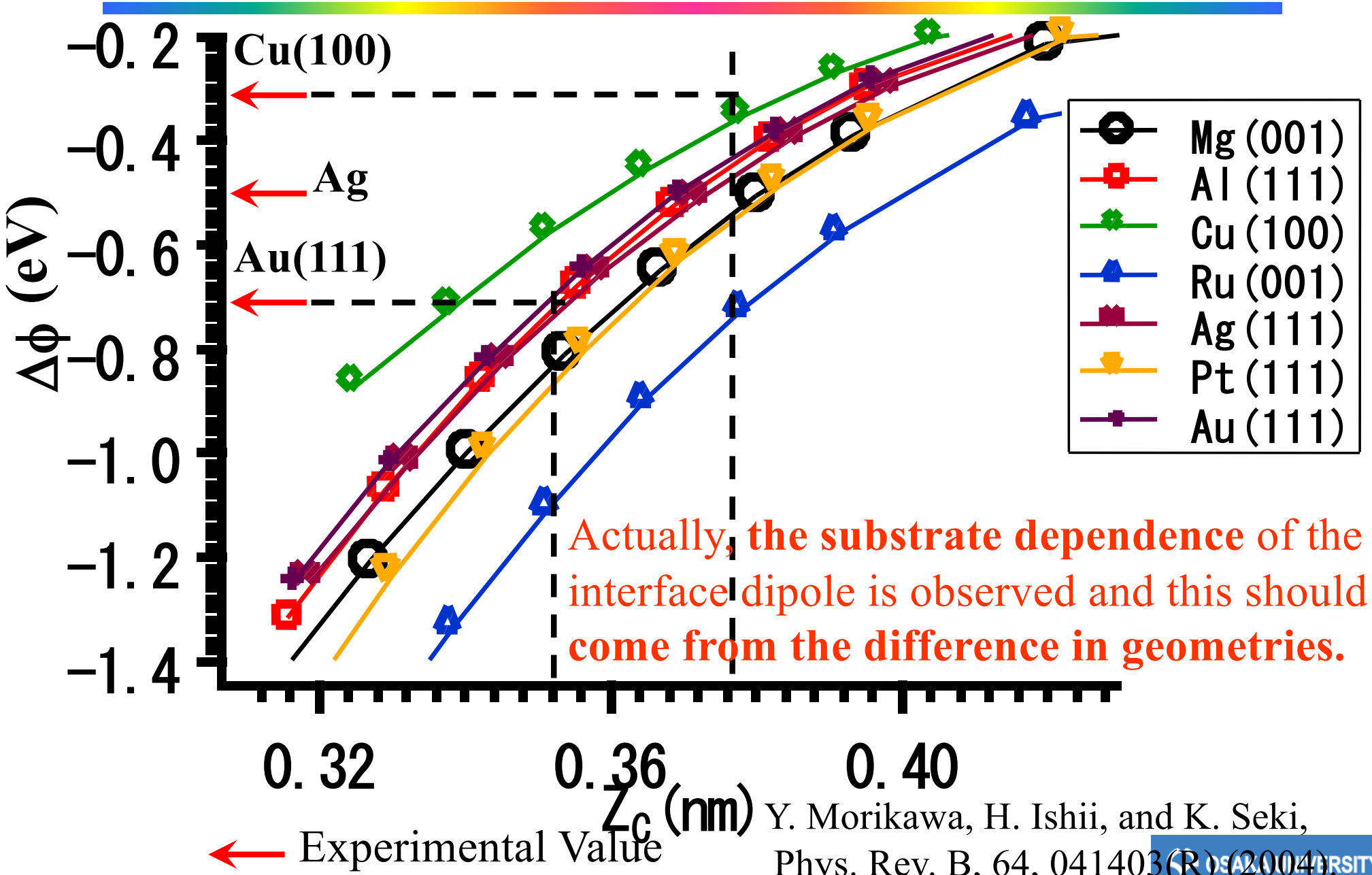

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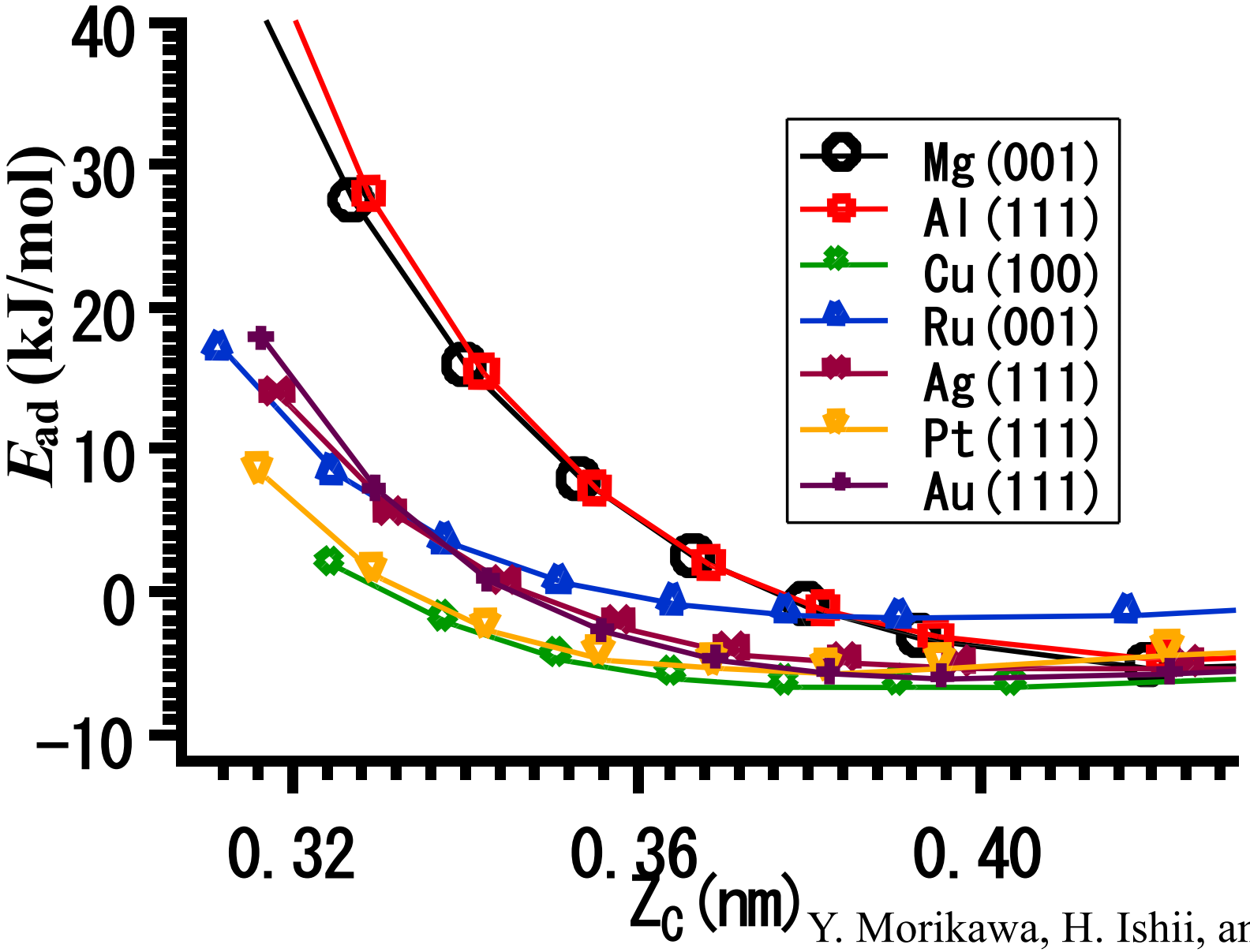
GGA Adsorption Energy: Butane on Metals



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DFT Calculations

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- DFT-GGA (PBE96)
- 長距離 van der Waals 相互作用

1) 半経験的な補正項 $-\sum_{ij}^{\text{atom pair}} f(R_{ij}) C_{ij} / R_{ij}^6$

DFT-D: S. Grimme, J. Comput. Chem. 27, 1787 (2006).

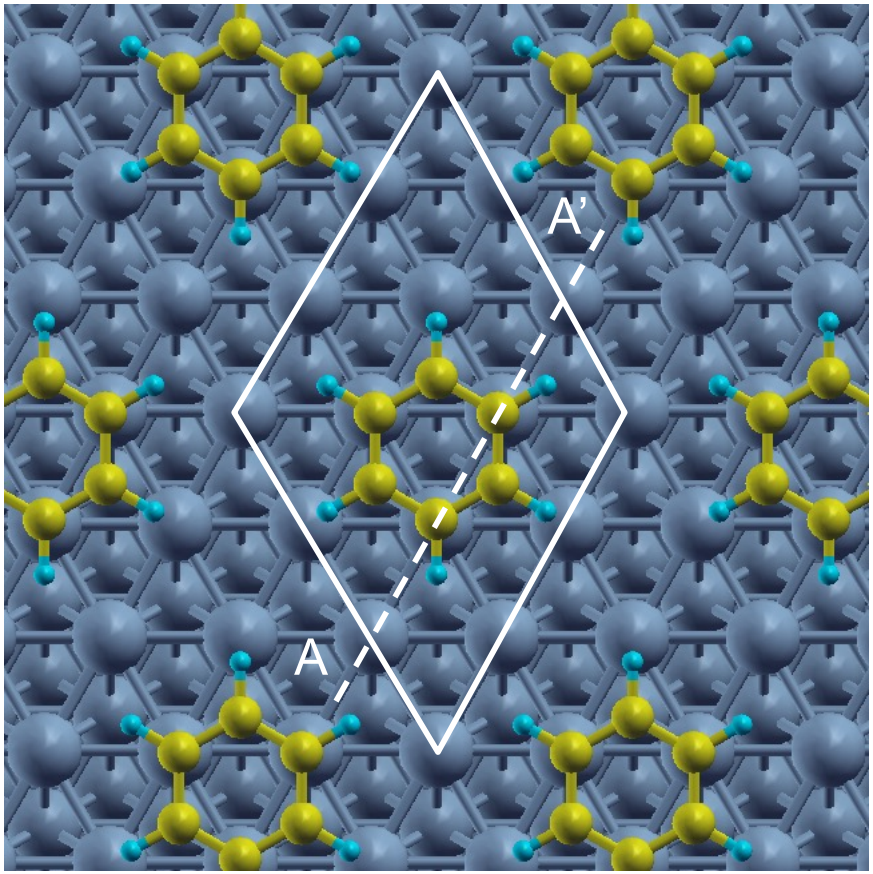
2) 長距離の電子相関を取り入れた汎関数

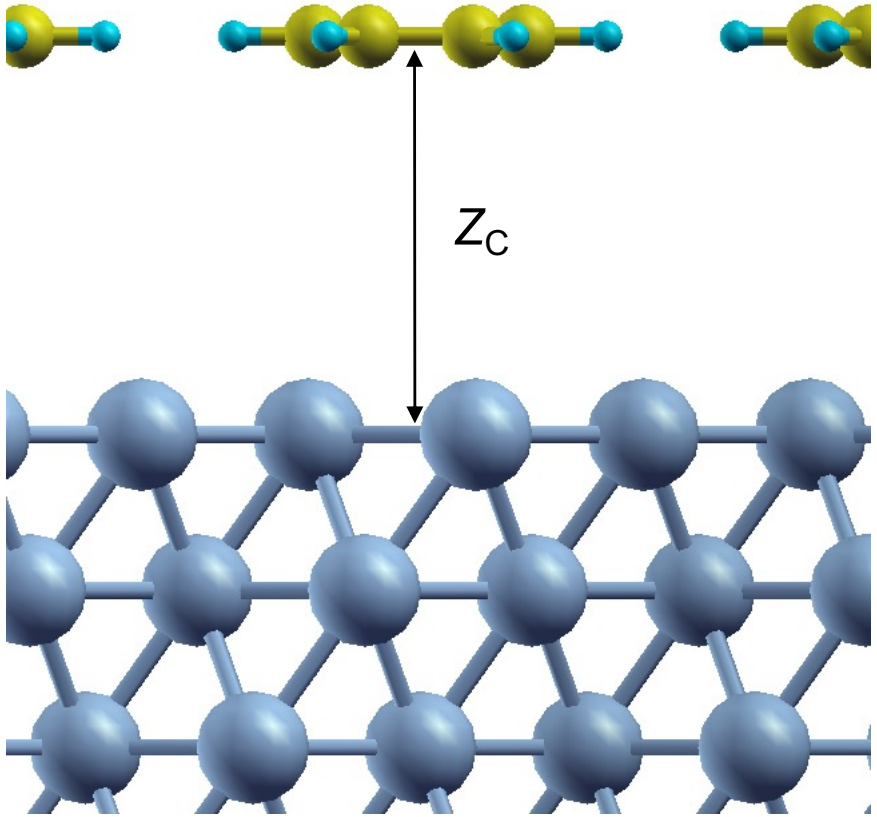
vdW-DF: M. Dion et al., Phys. Rev. Lett., 92, 246401 (2004).

Benzene/Noble Metals

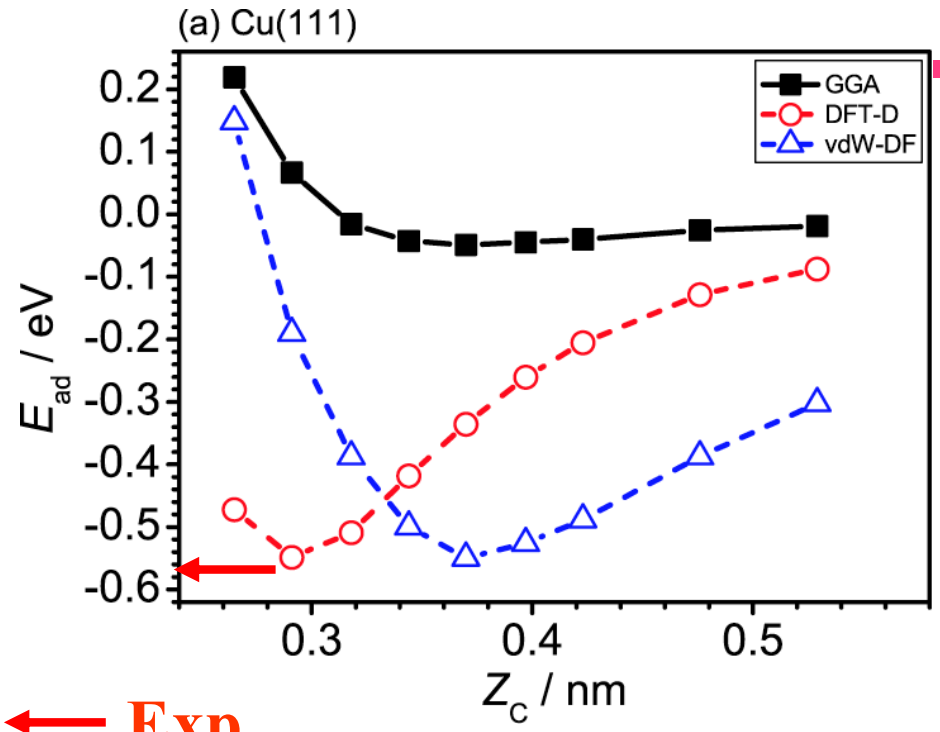
- K. Toyoda, Y. Nakano, I. Hamada, K.H. Lee, S. Yanagisawa, Y.M, Surf. Sci., **603**, 2912-2922 (2009).

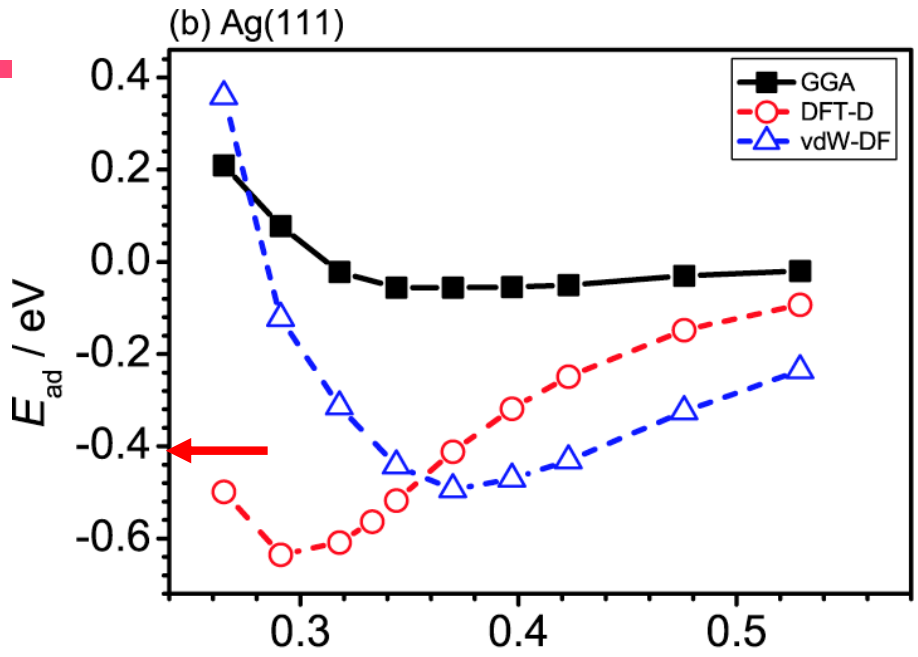
C_6H_6 on noble metals

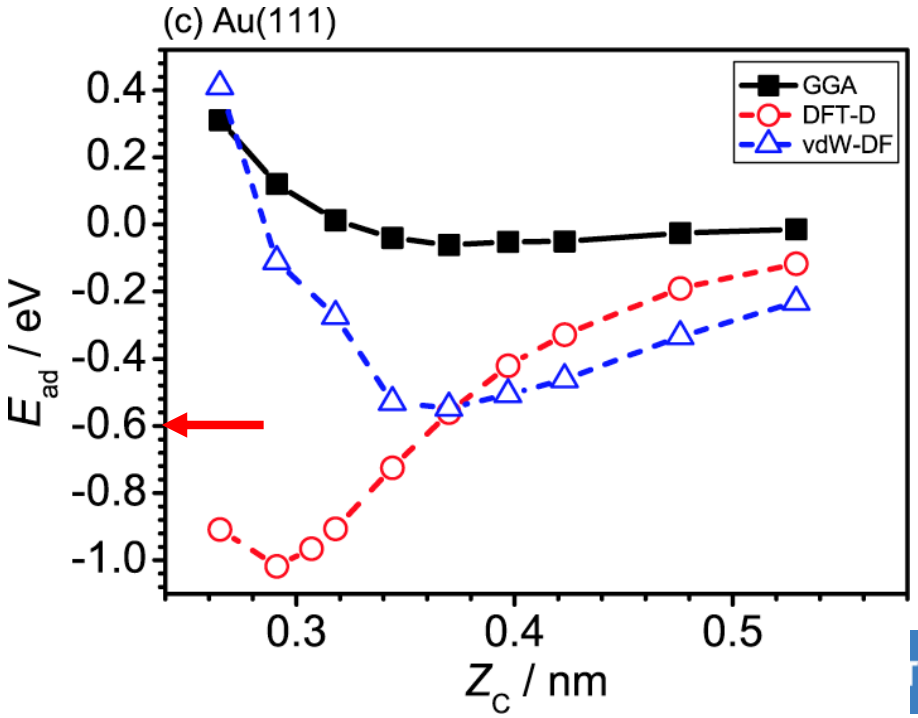




C_6H_6/Metals: Adsorption Energy



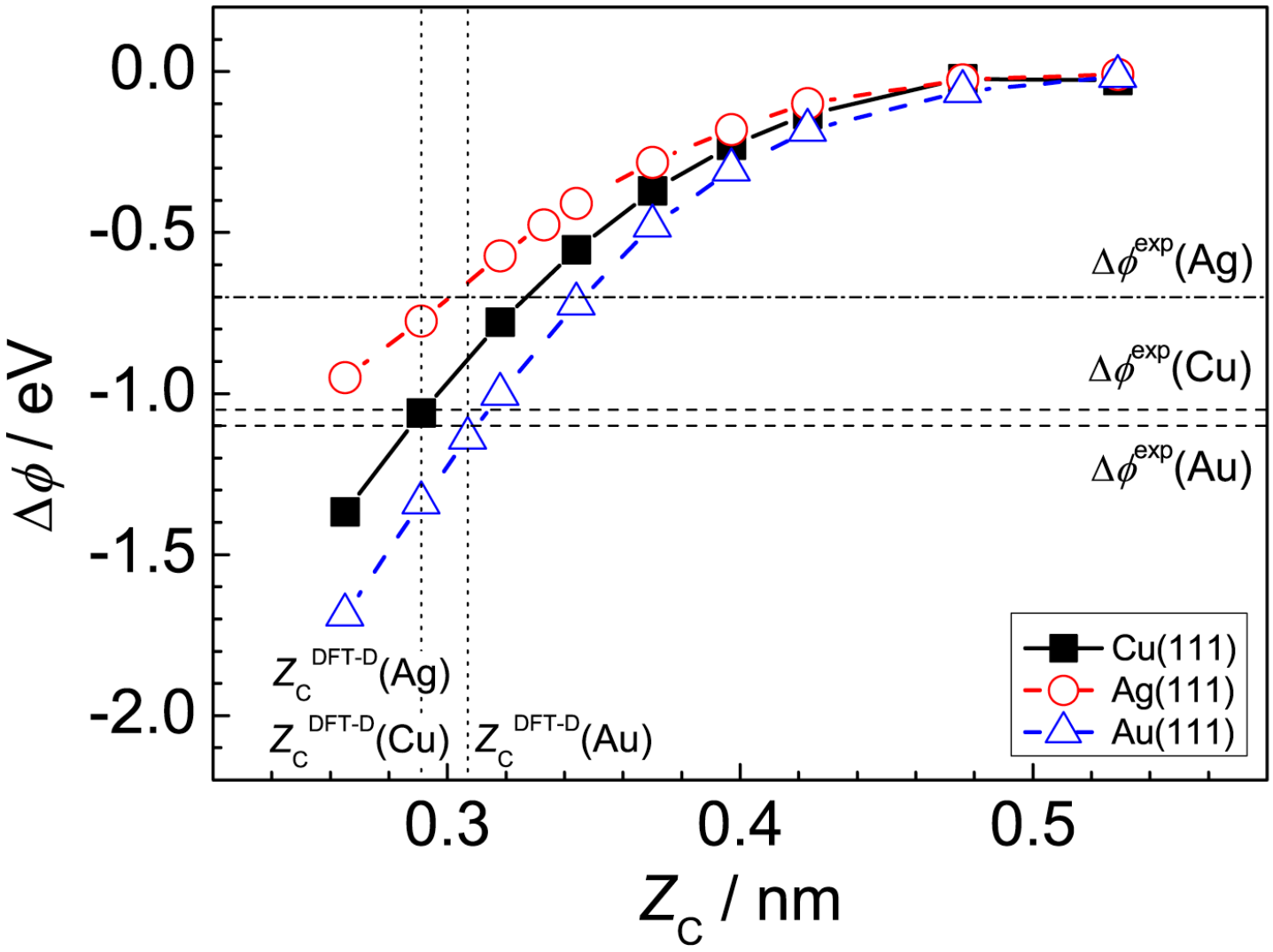




← **Exp.**

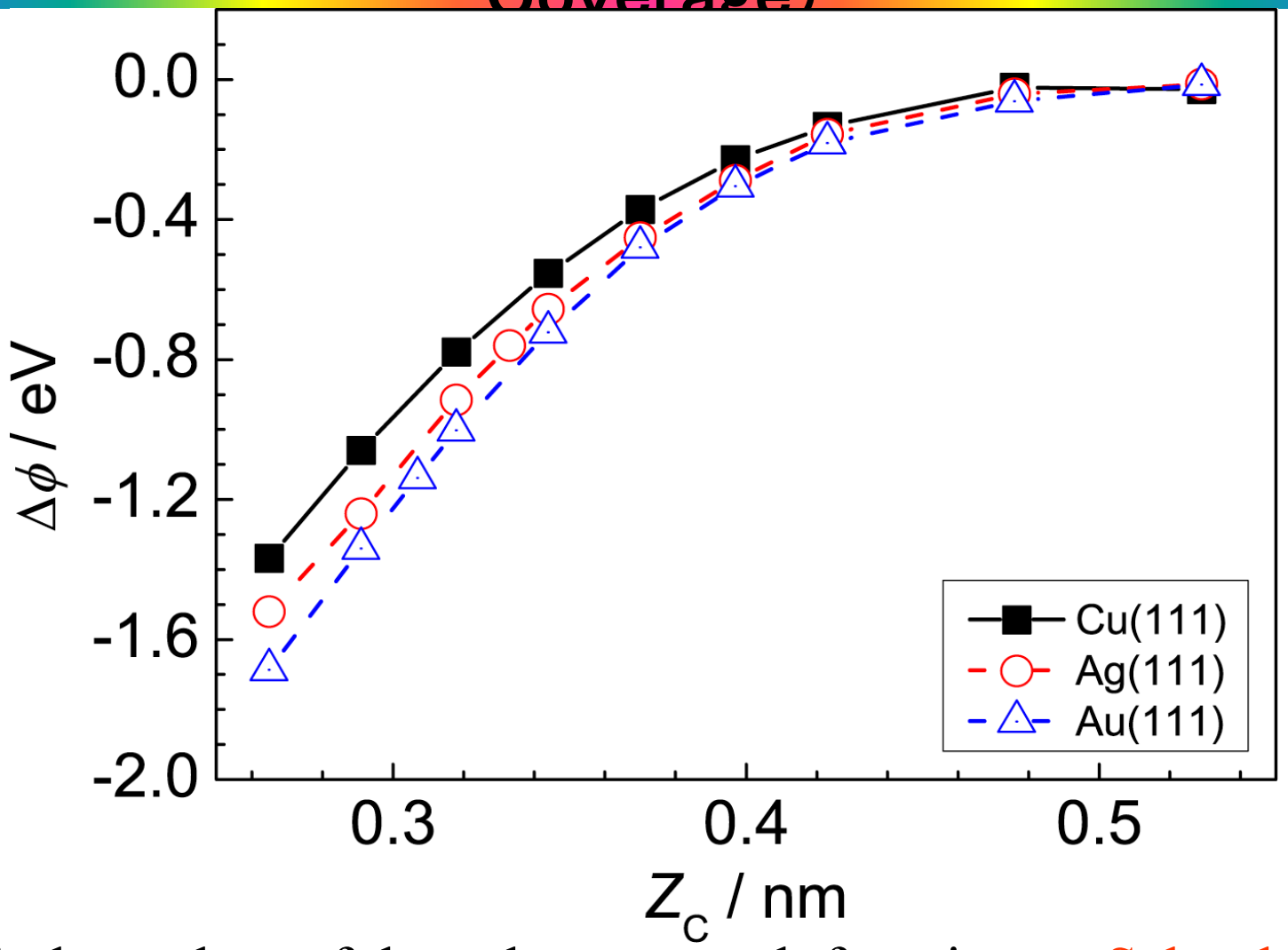
- vdW-DF gives reasonable energy
- DFT-D slightly over-estimate adsorption energies

C_6H_6/Metals: Work Function Change



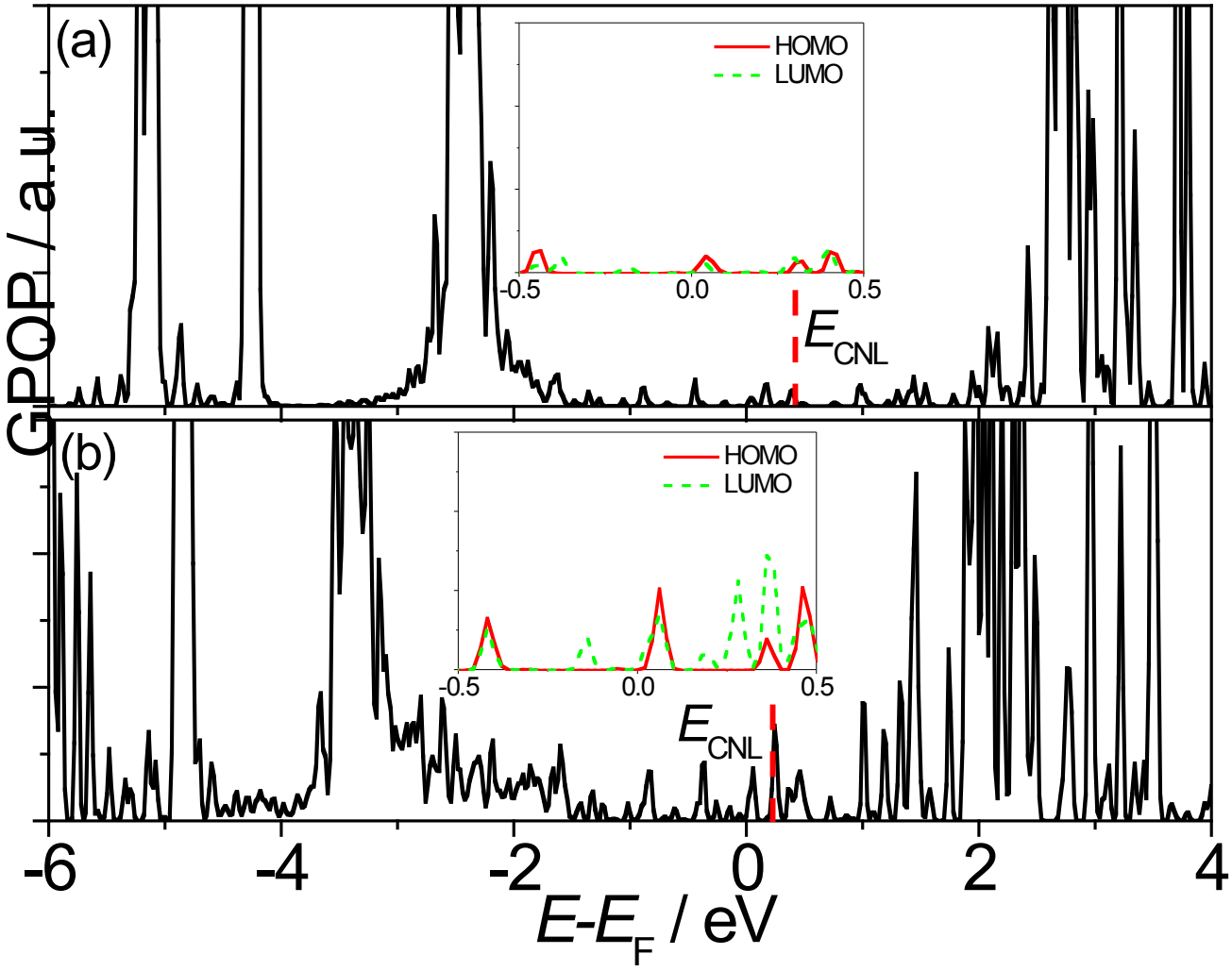
- Calculated work function changes using DFT-D optimized geometries agree quite well with the experimental results.

C_6H_6/Metals: Work Function Change (Same Coverage)



- $\Delta\phi$ is independent of the substrate work function=> Schottky Limit
- **Substrate dependence should come from the difference in geometries (metal-organic distances and coverage).**

C_6H_6/Cu(111): Gross Population

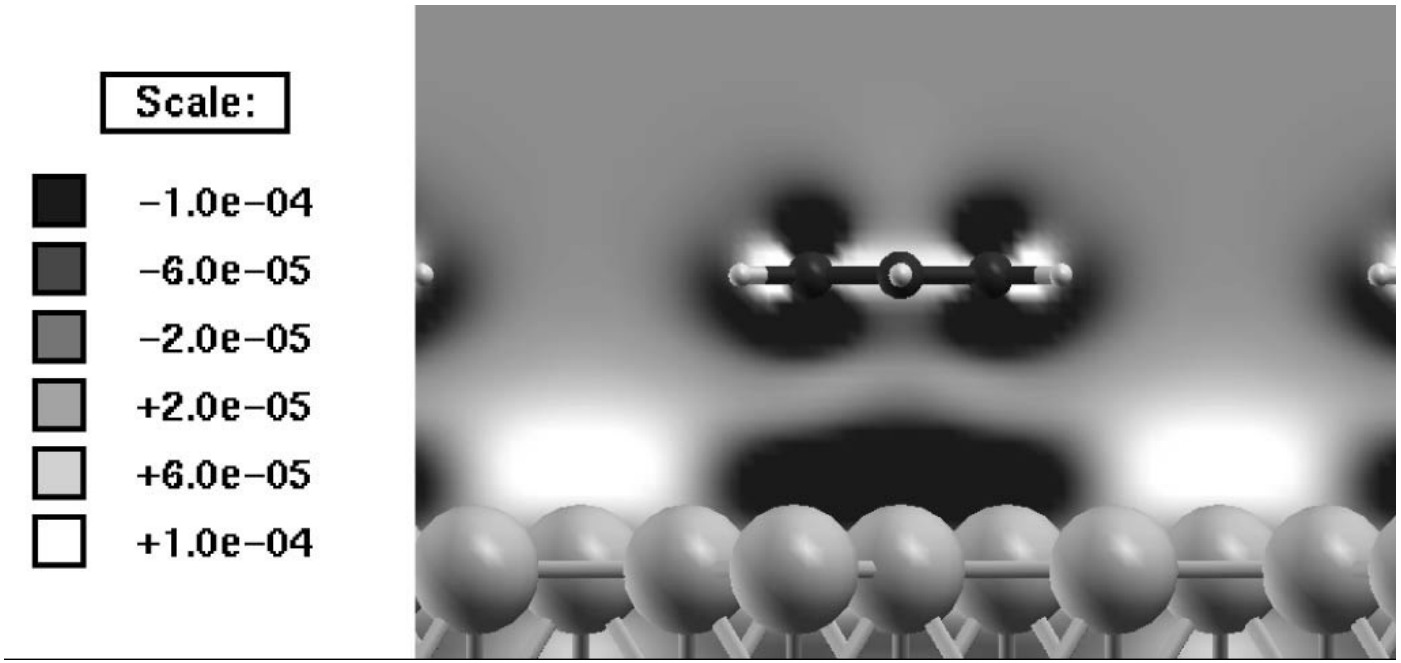


Z_C=0.37 nm

Z_C=0.29 nm

- Weak hybridization between MOs and substrate states.
- Small charge transfer from HOMO to the substrate.

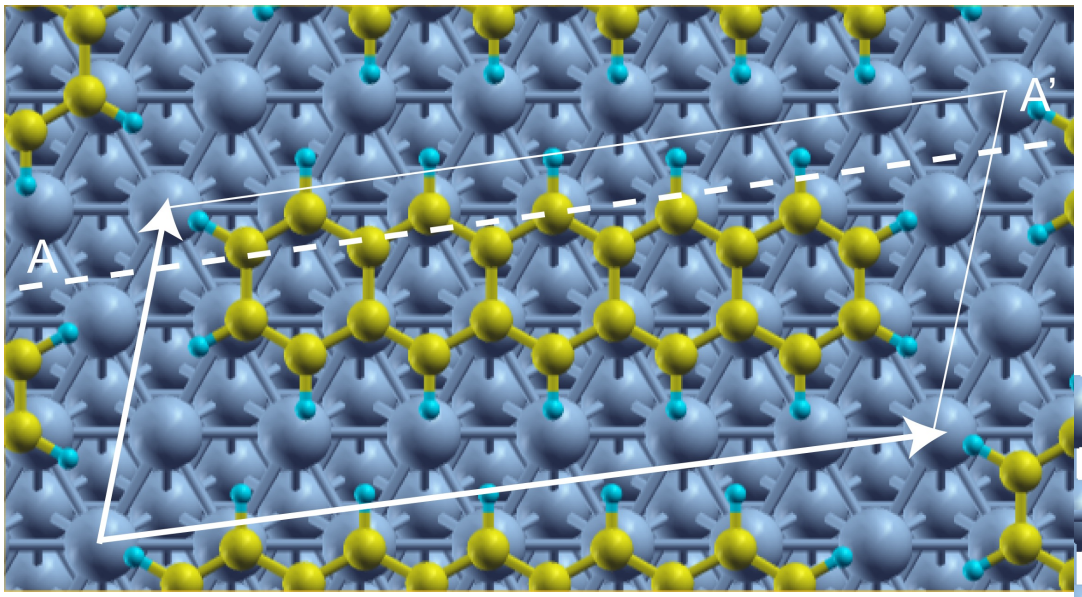
Difference Charge: C_6H_6/Al(111)

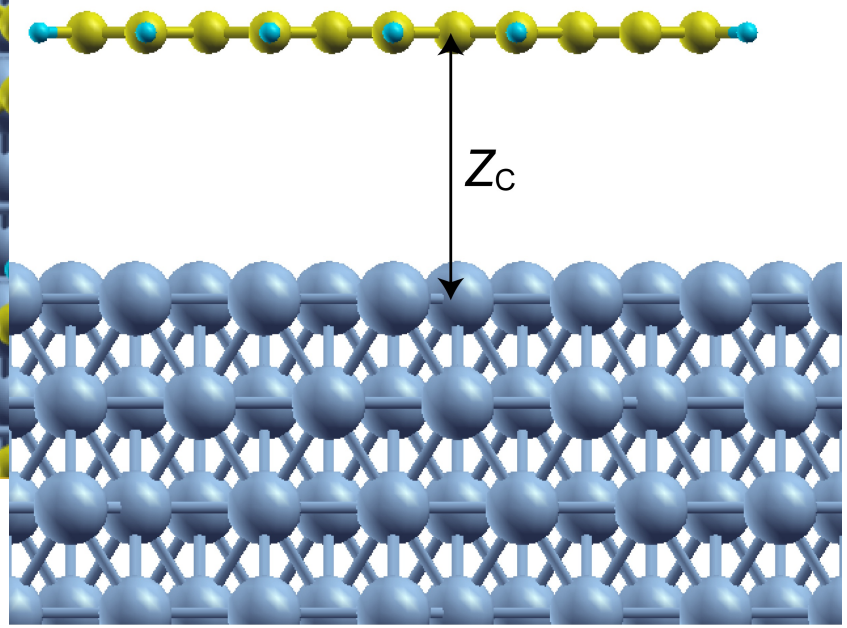


Pentacene/Noble Metals

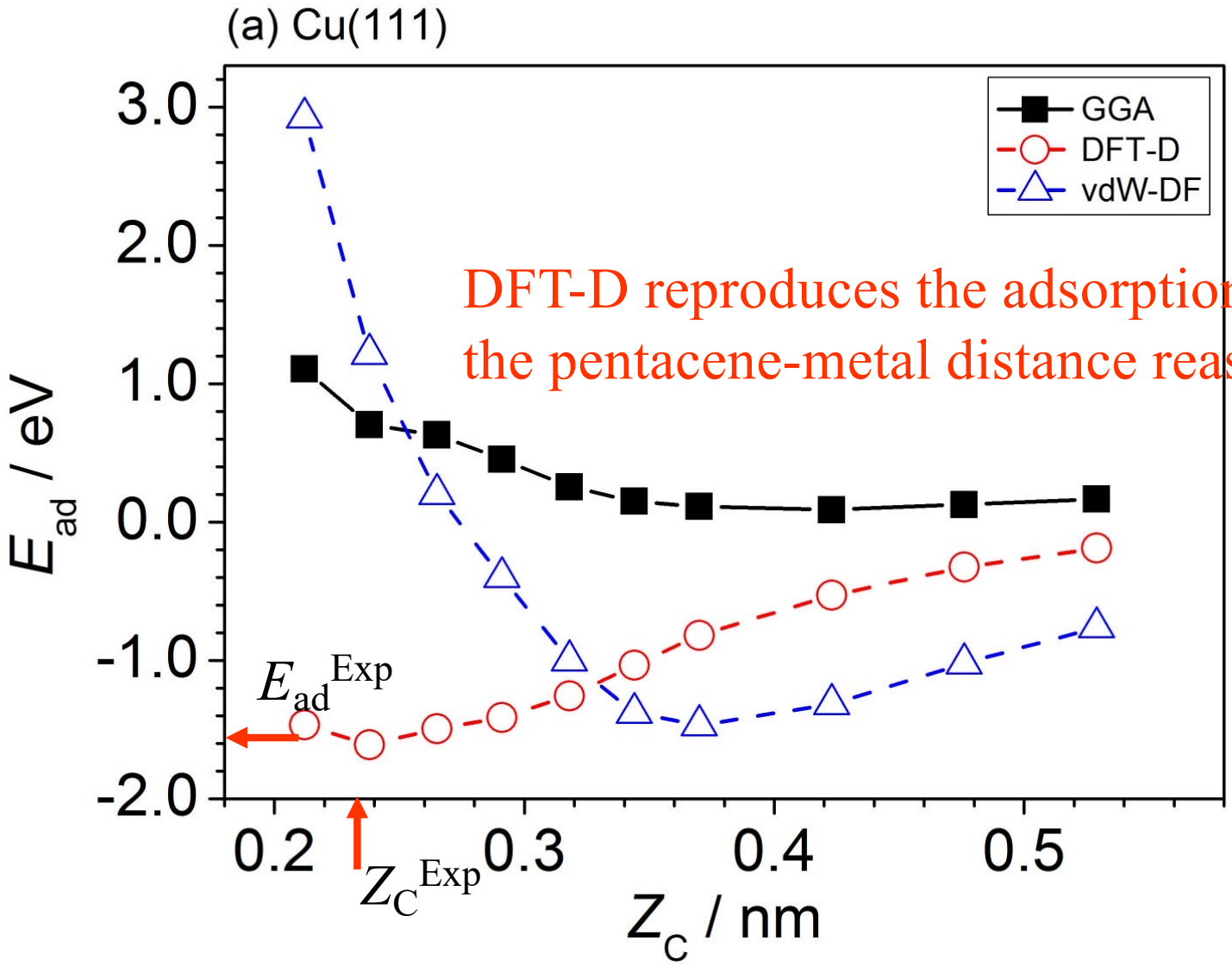
- K. Toyoda, Y. Nakano, I. Hamada, K.H. Lee, S. Yanagisawa, Y.M, J. Electron Spectrosc. Relat. Phenom., **174**, 78-84 (2009).
- K. Toyoda, I. Hamada, S. Yanagisawa, Y.M, Appl. Phys. Express, 3, 025701-1-3 (2010).
- K. Toyoda, I. Hamada, K.-H. Lee, S. Yanagisawa, Y.M, J. Chem. Phys., 132, 134703-1-9 (2010).

Pentacene/Cu(111)





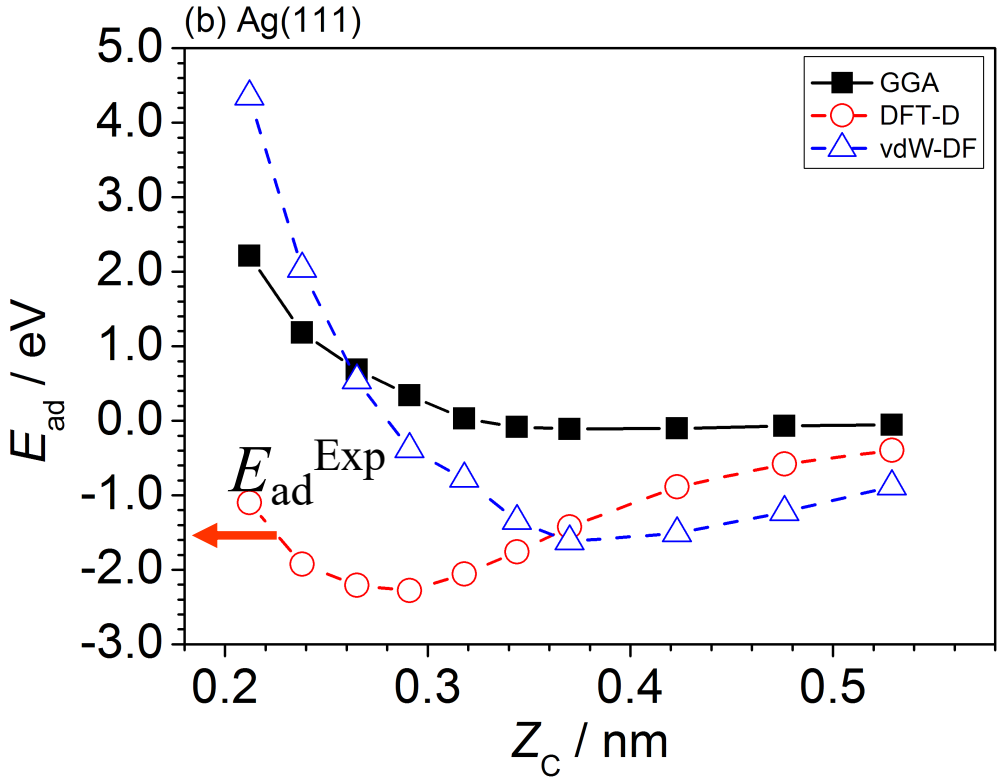
Pentacene/Cu(111): Adsorption Energy

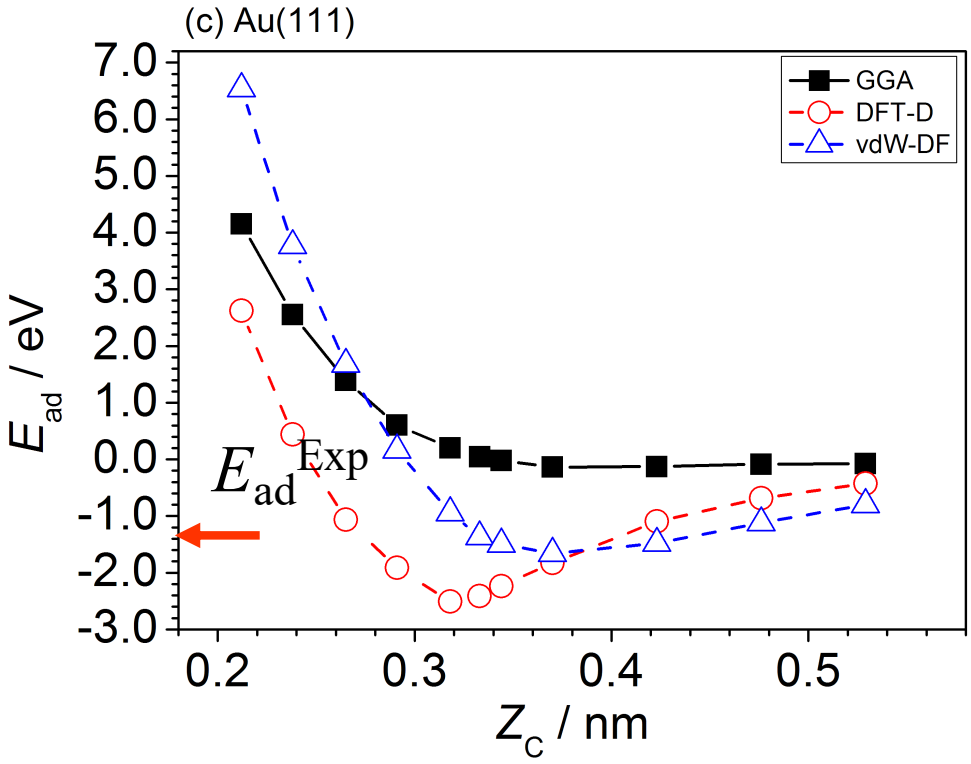


DFT-D reproduces the adsorption energy and the pentacene-metal distance reasonably well.

Exp: E_{ad}^{Exp} = -1.6 eV, Z_C^{Exp}=0.234nm, N. Koch et al., JACS **2008**, 130, 7300.

Pentacene/Cu(111): Adsorption Energy

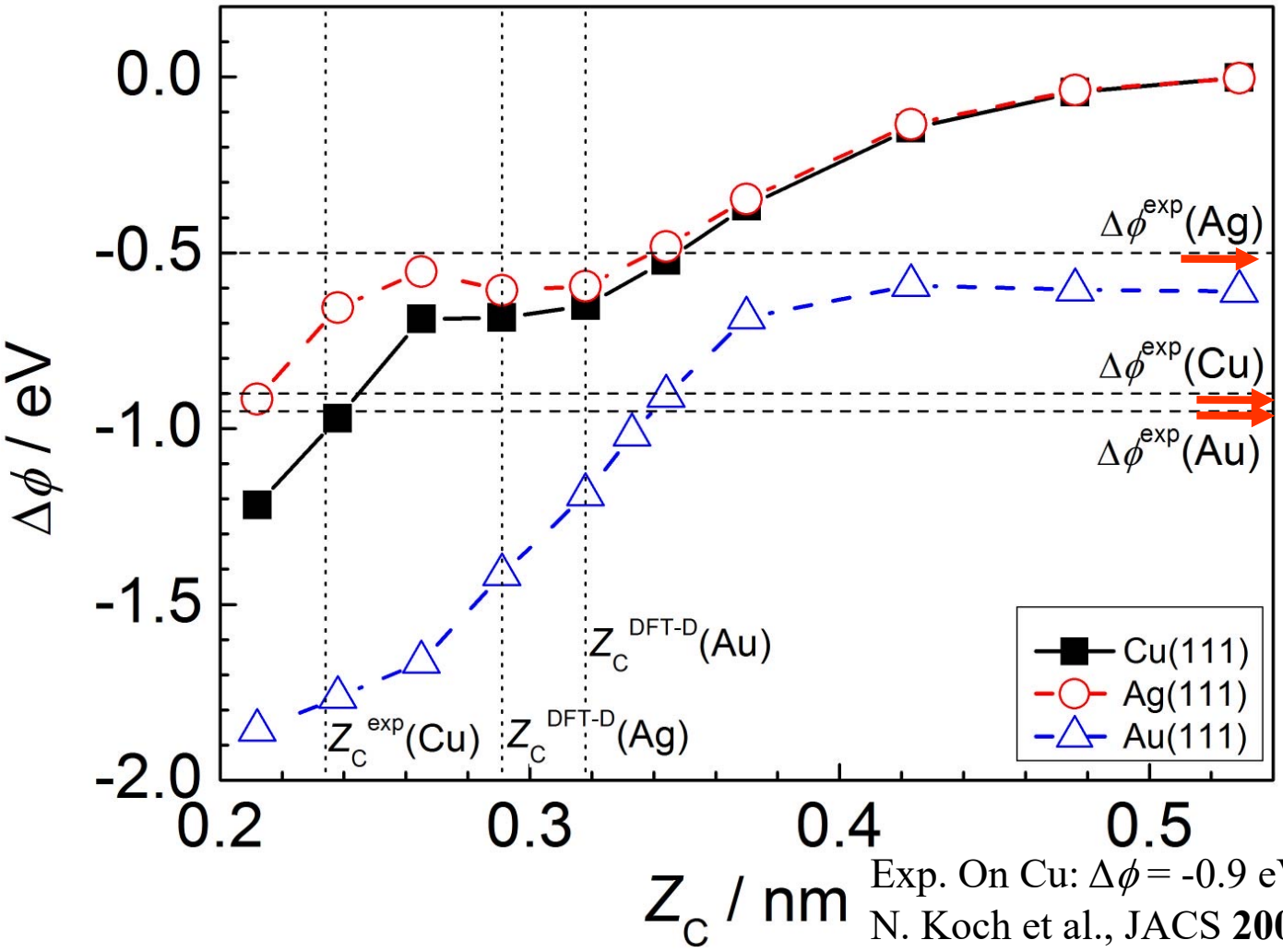




vdW-DF gives reasonable adsorption energyes while DFT-D overestimates them.

Pentacene/Cu, Ag, Au: Work Function Change

DFT-D reproduces the experimentally observed work function changes quite well.

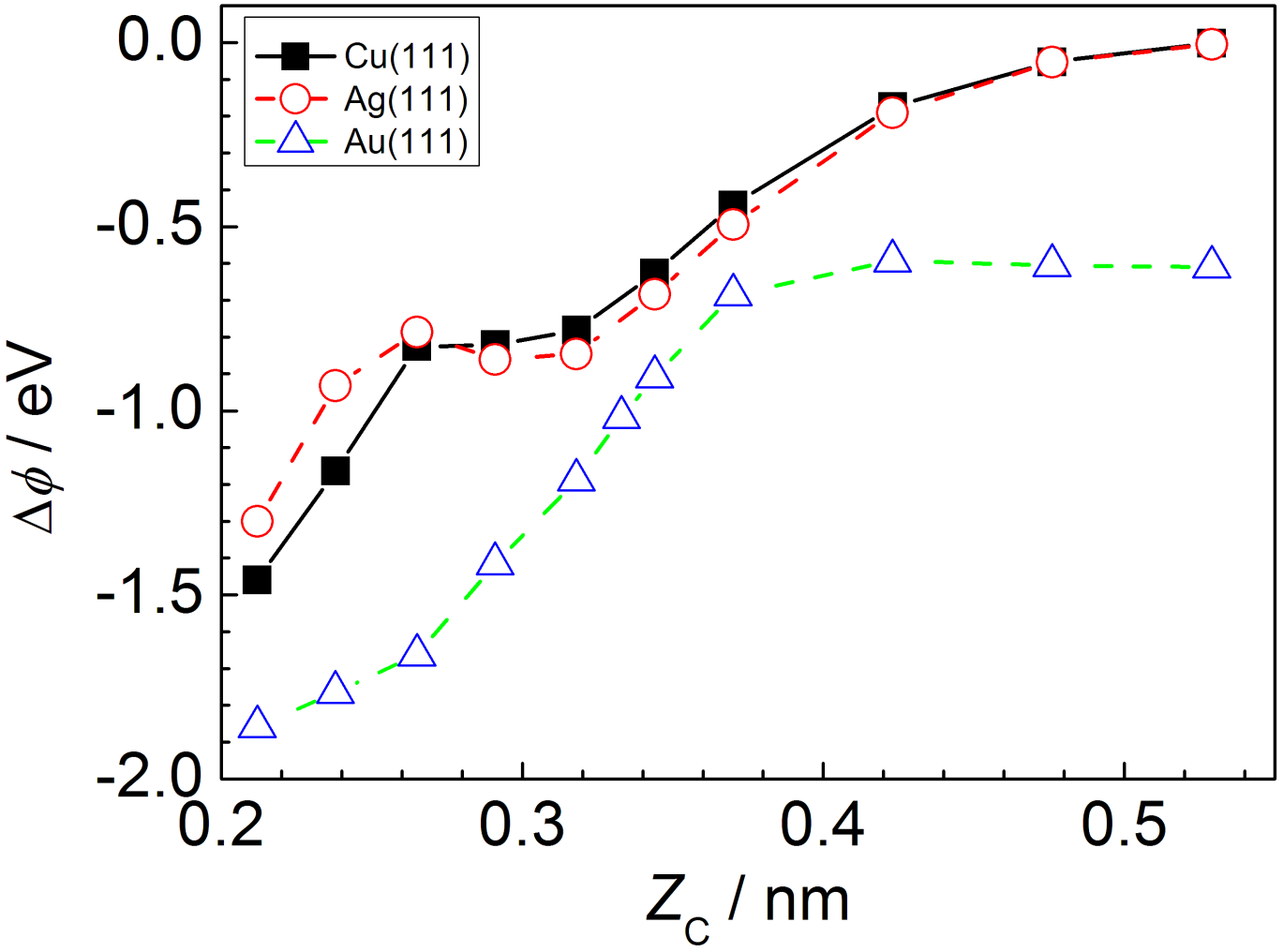


Exp. On Cu: $\Delta\phi$ = -0.9 eV, Z_C=0.234nm
N. Koch et al., JACS **2008**, 130, 7300.

Pentacene/Cu,Ag,Au: Work Function Change(Same Coverage)

Δϕ linearly depends on the substrate work function.
Bardeen Limit

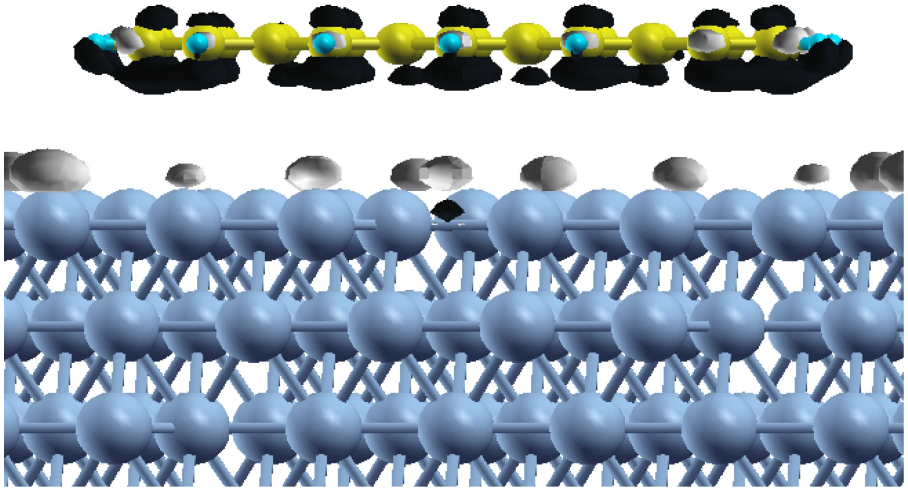
Δϕ is independent of the substrate work function.
Schottky Limit

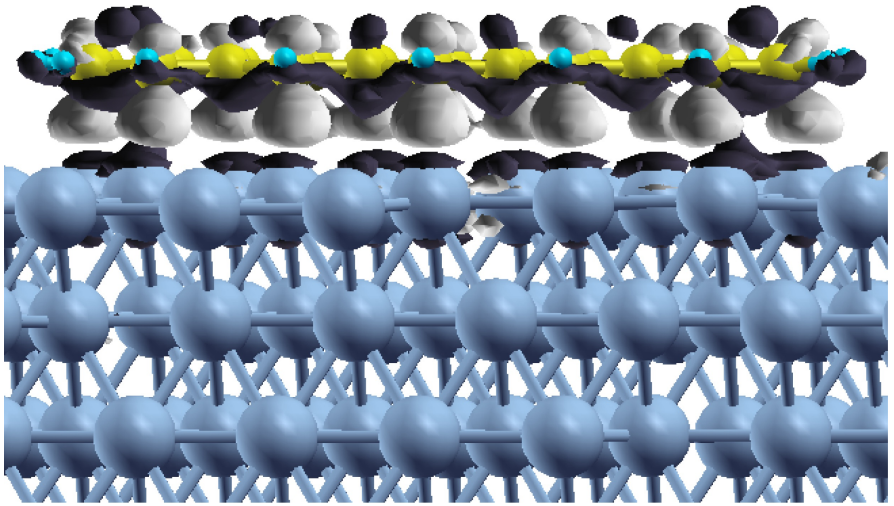


Difference Charge: Pen/Cu(111)

Z_C^{vdW}=0.37nm

Z_C^{exp}=0.24nm

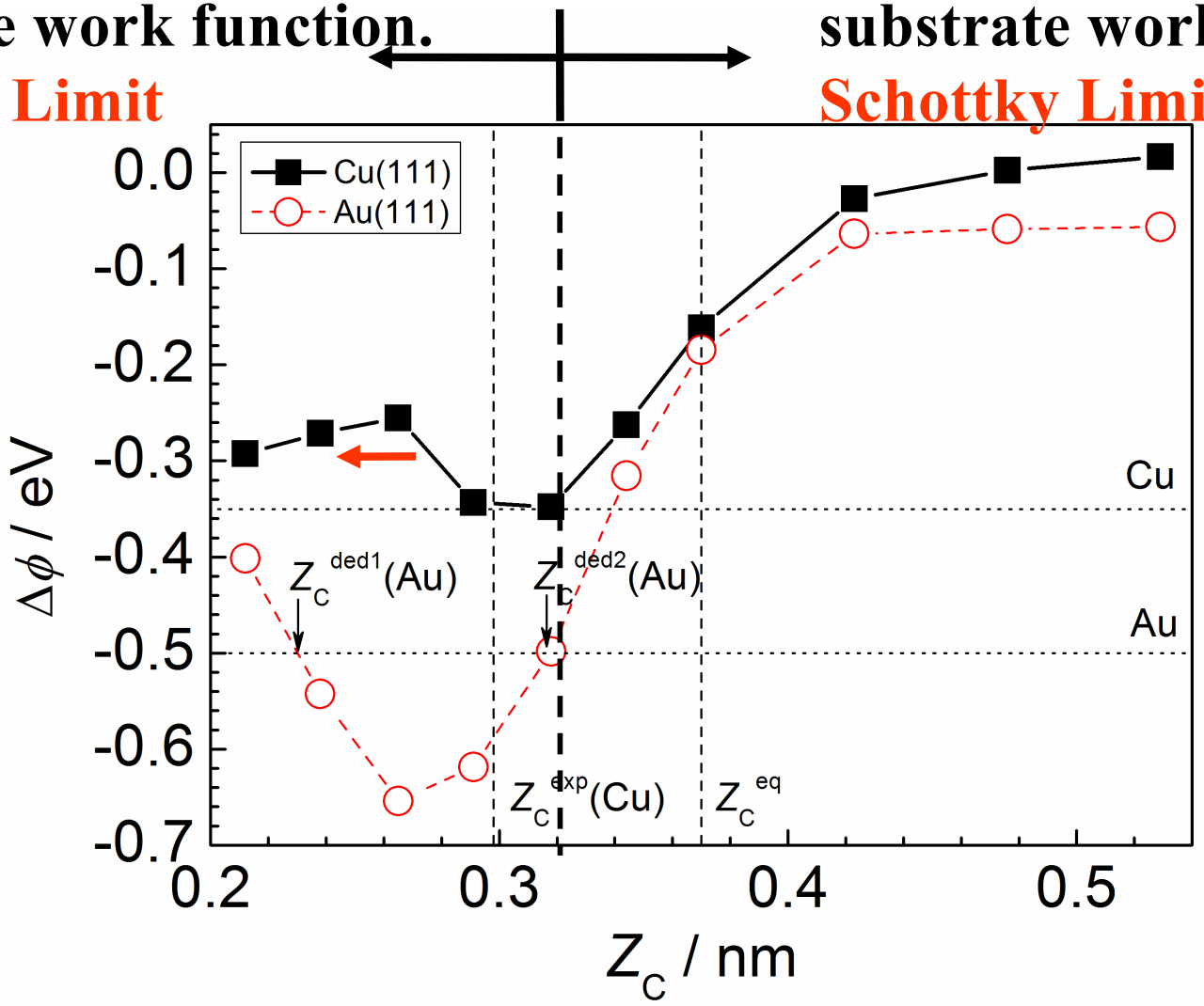




PFP/Cu, Au: Adsorption Energy

Δϕ linearly depends on the substrate work function.
Bardeen Limit

Δϕ is independent of the substrate work function.
Schottky Limit



Exp.: N. Koch et al., JACS 2008, 130, 7300.

Alq_3/Metals

- S. Yanagisawa, Y. M,
  Jpn. J. Appl. Phys, **45,** 413-416 (2006).
- S. Yanagisawa, Y. M,
  Chem. Phys. Lett., **420**, 523-528 (2006).
- S. Yanagisawa, K.H. Lee, Y. M,
  J. Chem. Phys.**128,** 244704-1-13 (2008).
- S. Yanagisawa, Y. M,
  J. Phys.: Condens. Matter **21,** 064247-1-6 (2009).

Alq_3/Al Interfaces

- Alq_3: Most widely used electron transport and emission material in organic EL devices.
- Interface state is observed.

  Shen et al., J. Appl. Phys. 89 (2001) 449.

→Strong Chemical Interactions

- Interfacial Dipole Layer: −1.4eV

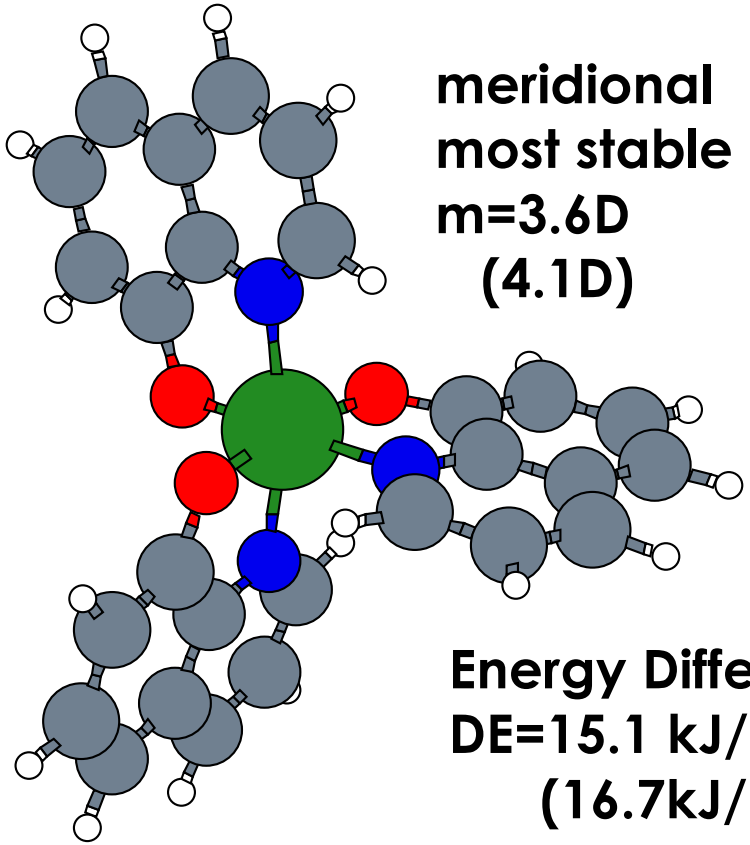
  Yokoyama et al., Jpn. J. Appl. Phys. 42 (2003) 3666.
- First-principles Simulation

  Curioni et al., Synth. Met. 111-112 (2000) 299.

→Physical Interaction.

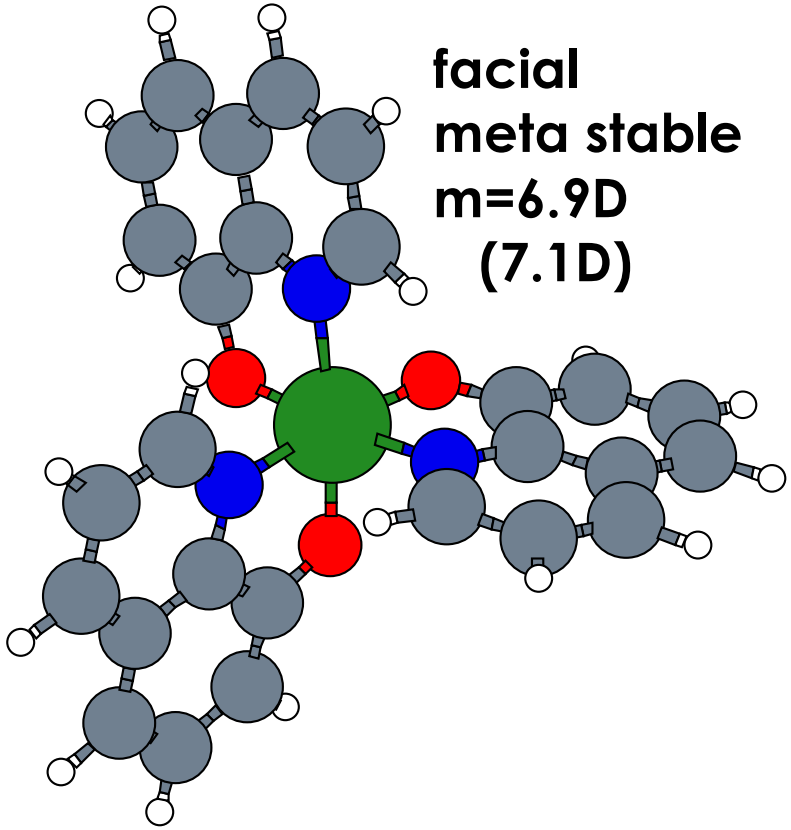
→No discussion on the Interfacial Dipole

Alq_3 Molecular Structure



meridional
most stable
m=3.6D
(4.1D)

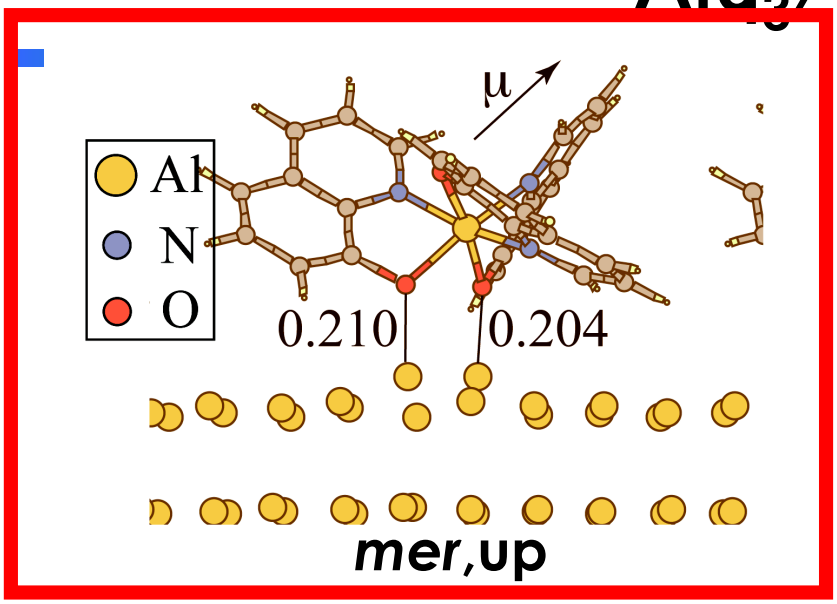
Energy Difference
DE=15.1 kJ/mol
(16.7kJ/mol)



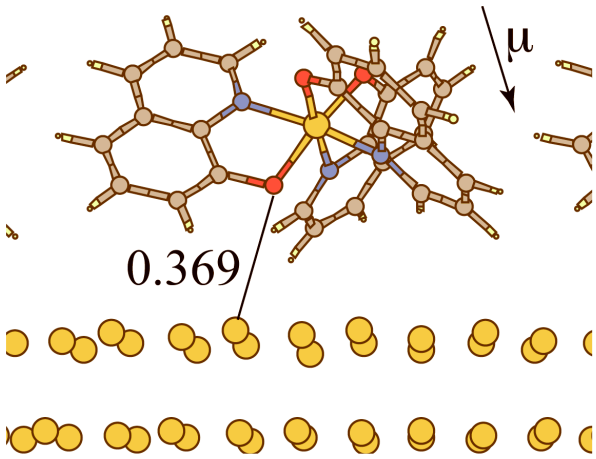
facial
meta stable
m=6.9D
(7.1D)

Values in parenthesis:
Curioni, Boero, Andreoni, Chem. Phys. Lett. 294 (1998) 263.

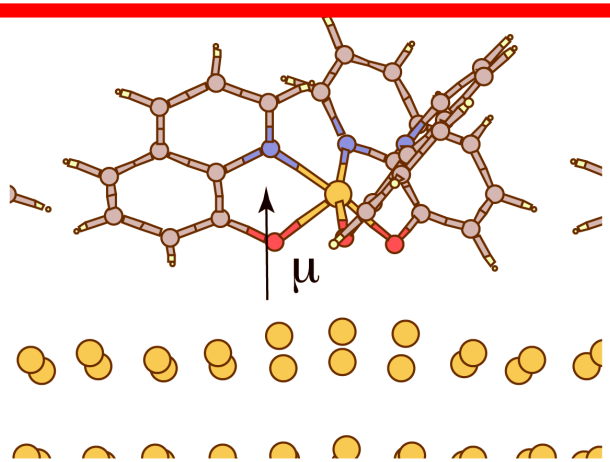
Alq_3/Al(111)



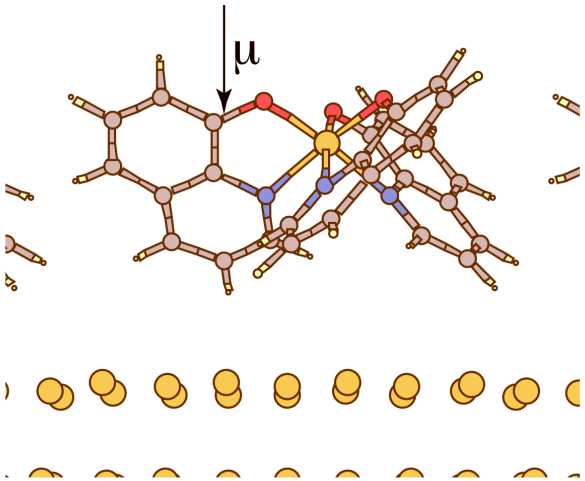
mer,up



mer,down



fac,up, most stable



fac,down

Adsorption Energy

(kJ/mol)		mer/up	mer/down	fac/up	fac/down
Al(111)	GGA	-57.9	-42.1	-7.7	-68.5
	LDA	126.9	83.4	199.1	68.8
	vdW	69.8	77.6	101.1	40.5
Al(332)	GGA	-8.1	-15.7	63.9	-71.1
	LDA	150.7	57.4	239.1	38.3
	vdW	193.1	184.9	257.7	143.8
Al adatom /Al(111)	GGA	46.9	-25.0	85.5	-114.6
	LDA	191.8	149.5	239.5	63.4
	vdW	113.0	79.9	158.4	-18.4

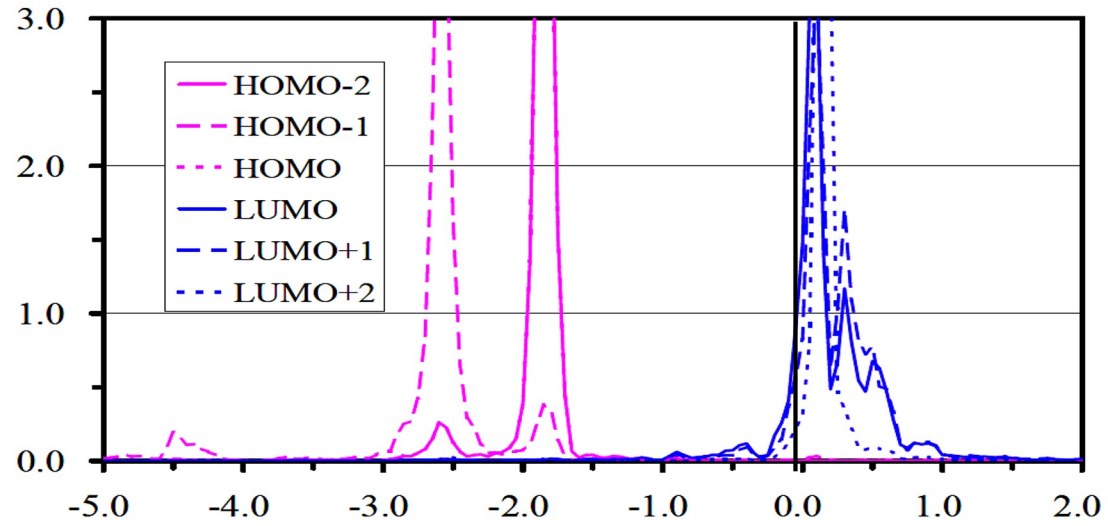
- Upward configurations are more stable than downward configurations.

Interfacial Dipole

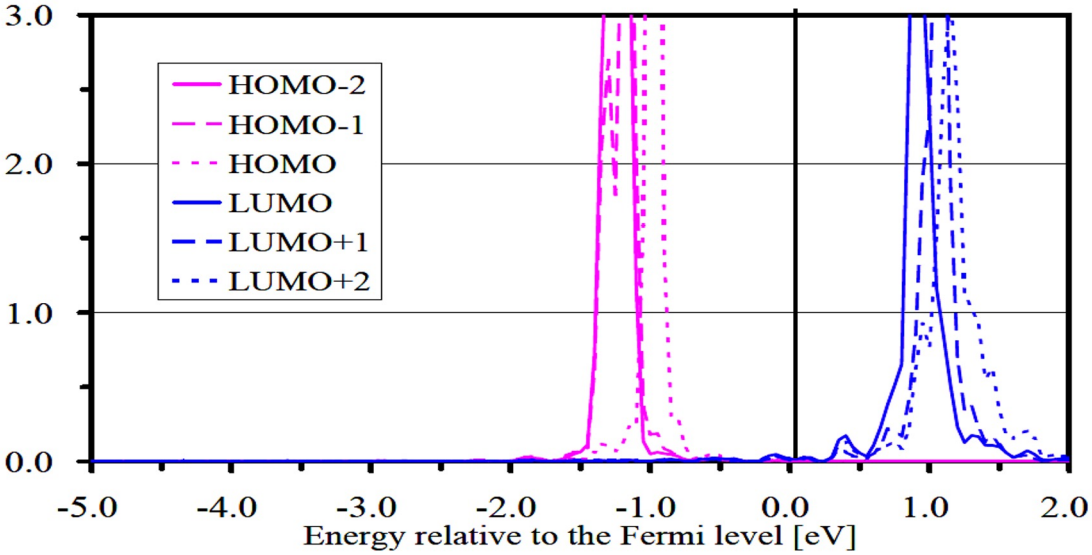
Δ/eV	mer/up	mer/down	fac/up	fac/down
Al(111)	−1.2	+0.1	−1.5	+1.2
Al(332)	−1.0	+0.0	−1.3	+0.8
Al adatom /Al(111)	−1.4	−0.7	−1.6	+0.8

- The work function change of -1.0～-1.6 eV agrees well with experimental observation of -1.4 eV.
- The interfacial dipole mainly comes from molecular permanent dipole.

Projected Density of States

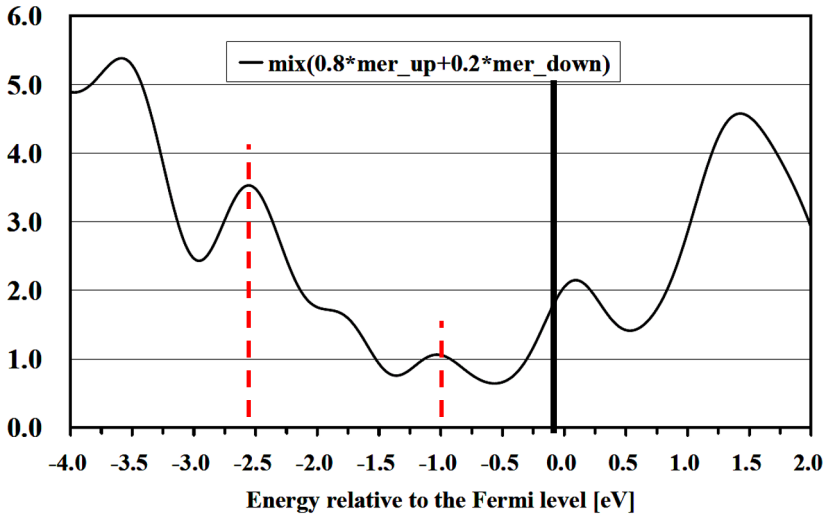


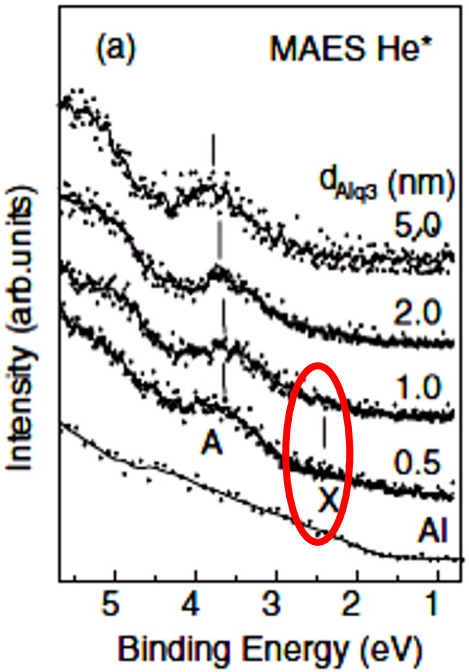
Alq_3(mer, up)/Al(111)

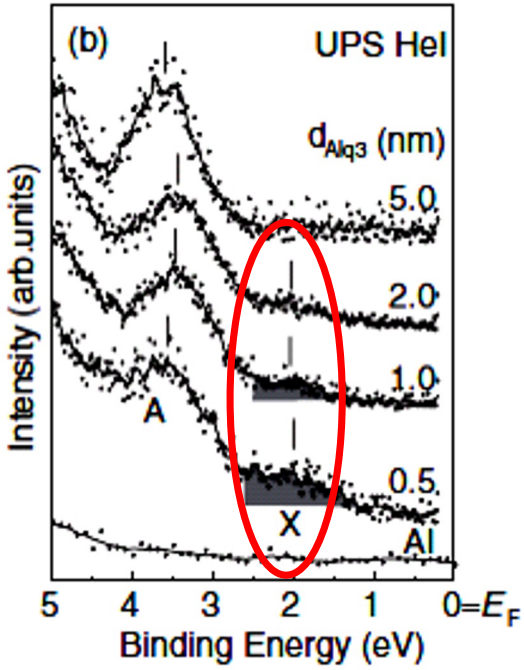


Alq_3(mer, down)/Al(111)

Mer/up and mer/down coexist







まとめと今後の展望

- 界面の電子状態、電子準位接続は界面の構造にきわめて敏感に依存する。
- 有機/金属界面の構造は、弱い長距離ファンデルワールス相互作用の影響が強く、非常にフレキシブルなため構造が変わりやすい。
- 弱い相互作用が支配的な系についても、界面原子構造と電子状態の第一原理による半定量的予測が可能となってきている。
- 今後、これらの手法により、界面電子準位接続を制御する指針を与えることが可能となった。