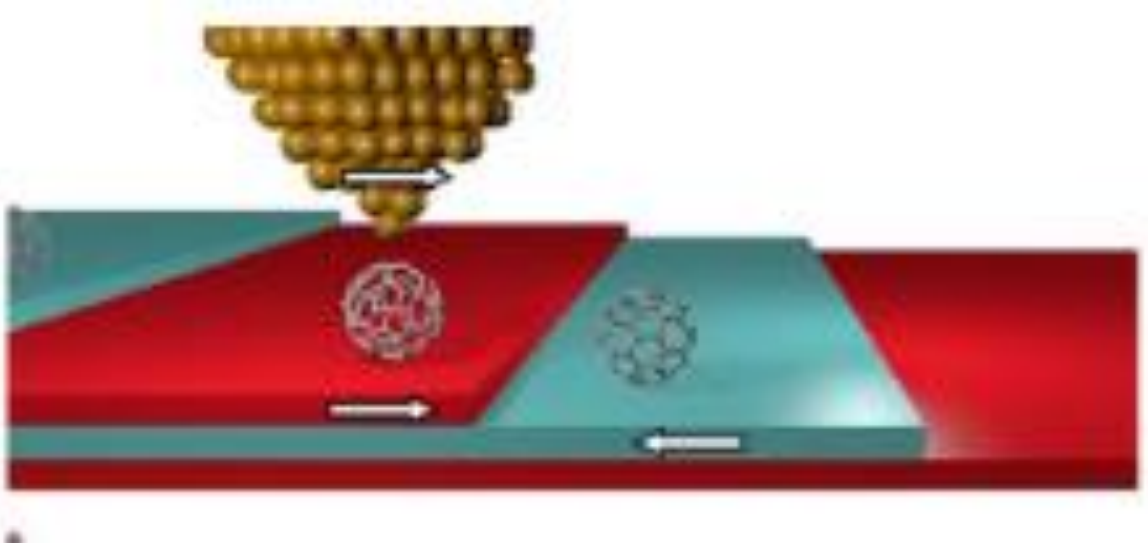
DE LA RECHERCHE À L'INDUSTRIE

CONCEPTS AND MODELLING TOOLS IN MOLECULAR SPINTRONICS



Cyrille Barreteau

Paris, 17-20 December 2018

ACKNOWLEDGEMENTS
COLLABORATIVE NETWORK

Alexander Smogunov, Yannick Dappe, Dongzhe Li, Ludovic Le Laurent

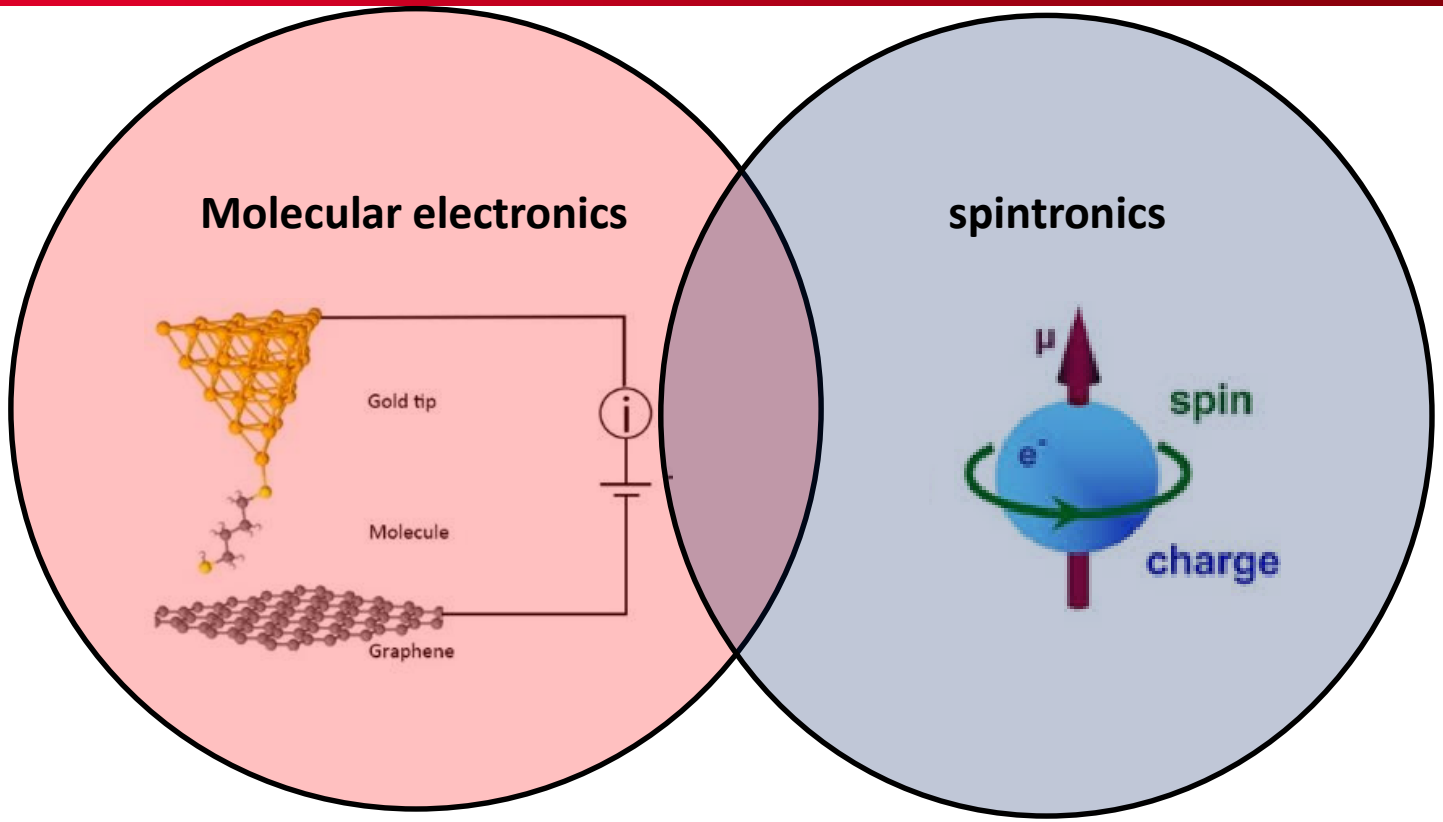
Vincent Repain, Amandine Bellec, Jérôme Lagoute, Kaushik Bairagi, Cynthia Fourmental ..

Shobhana Narasimhan, Sourav Mondal, Rajdeep Banerjee

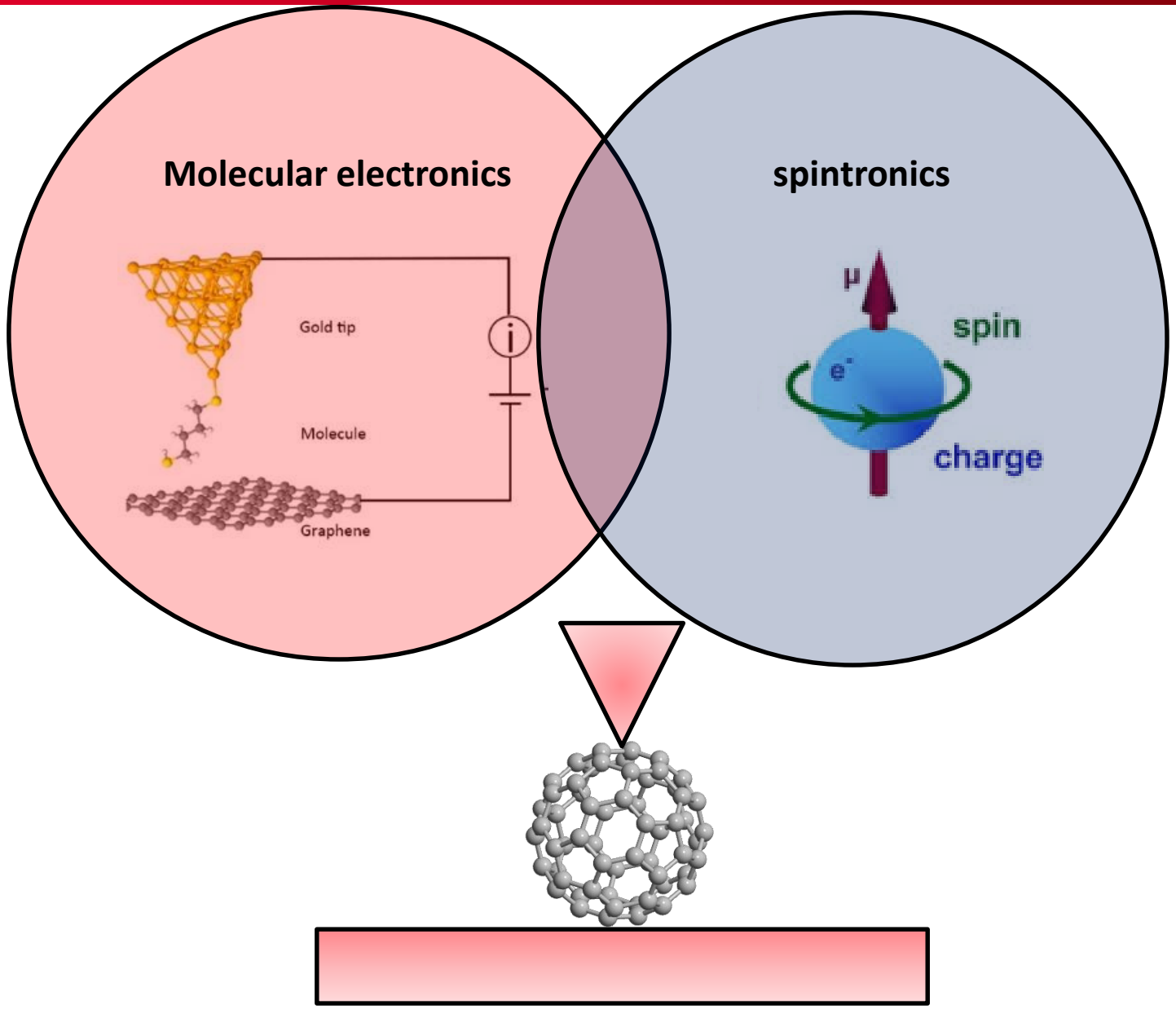
Talal Mallah, Marie-laure Boillot

INTRODUCTION

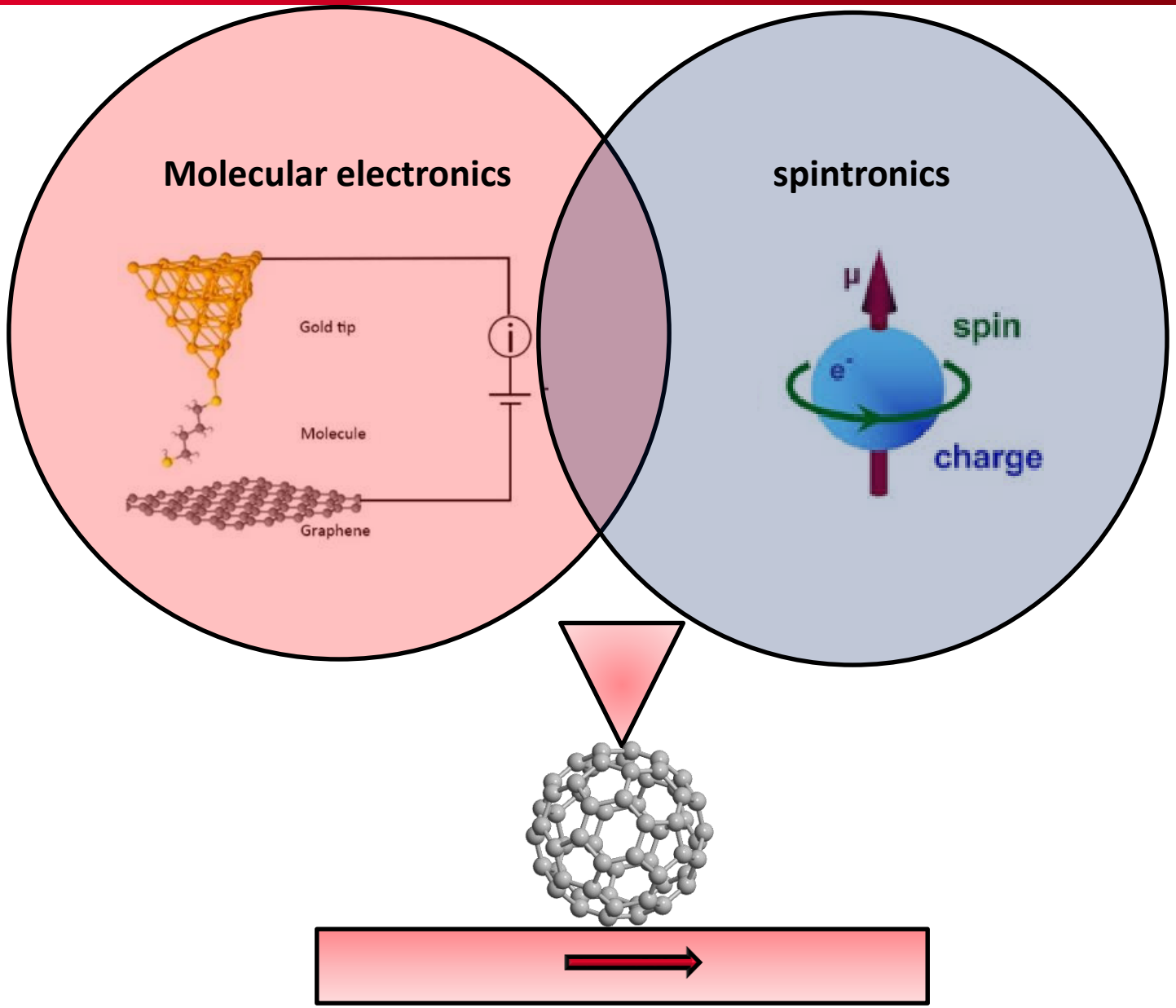
MOLECULAR SPINTRONICS



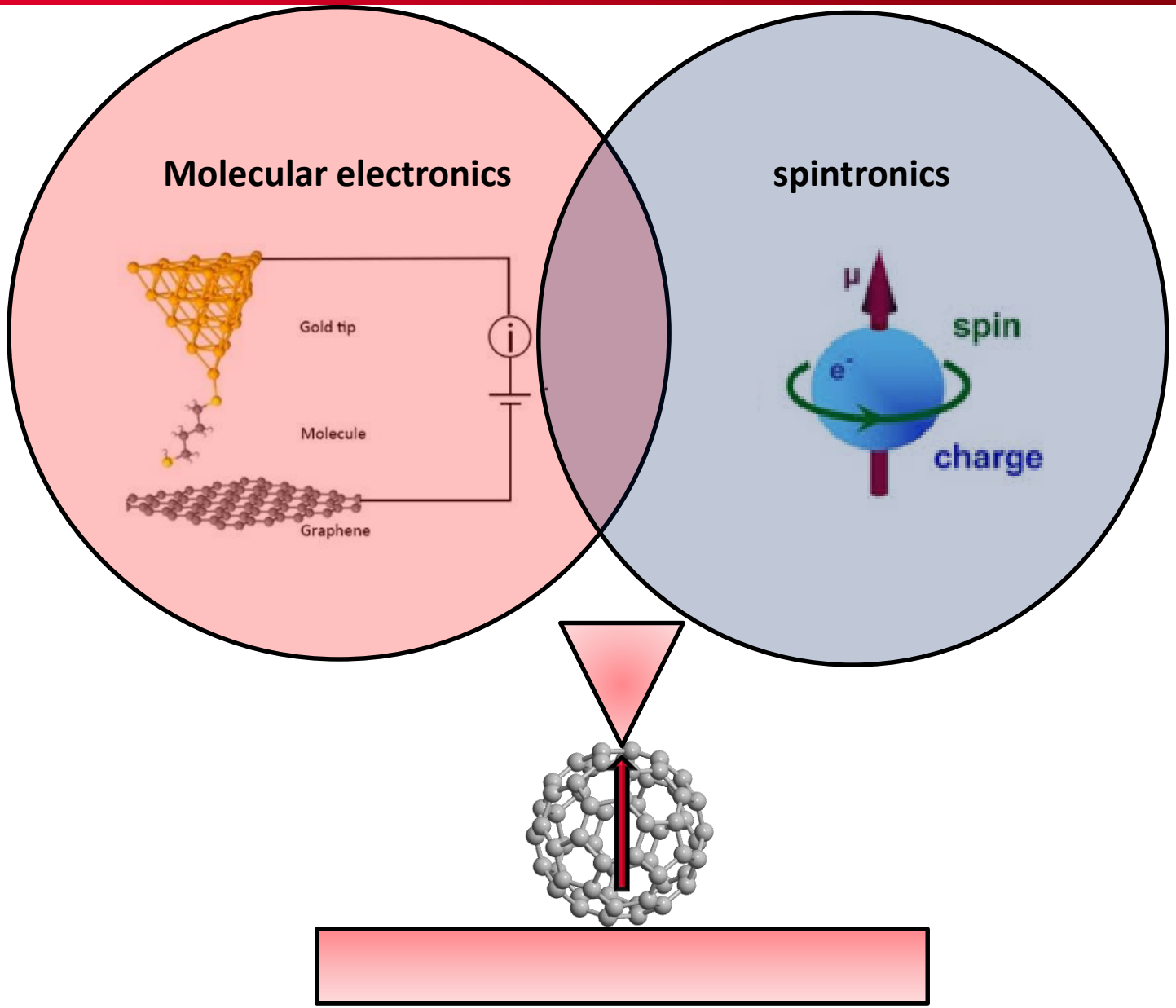
MOLECULAR SPINTRONICS



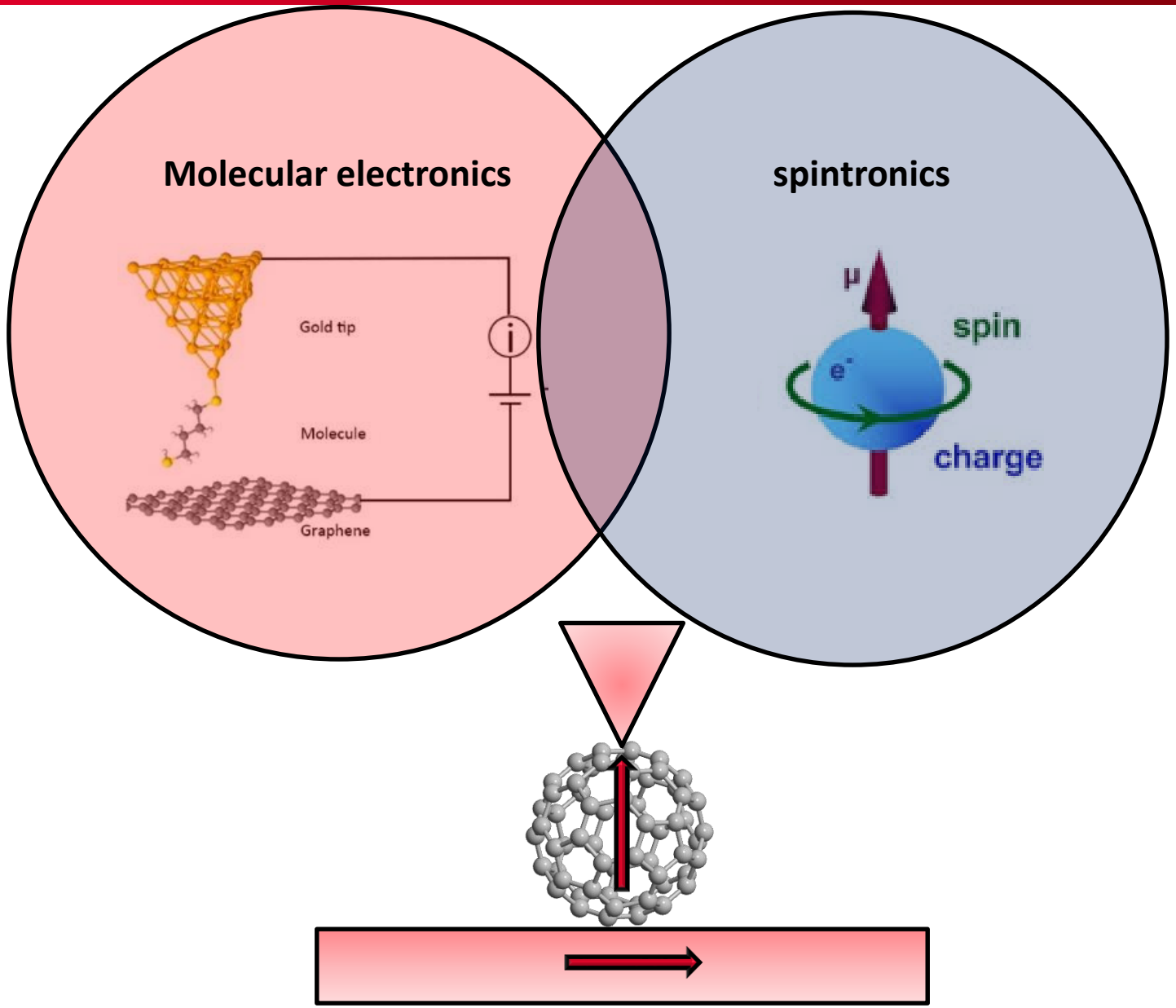
MOLECULAR SPINTRONICS



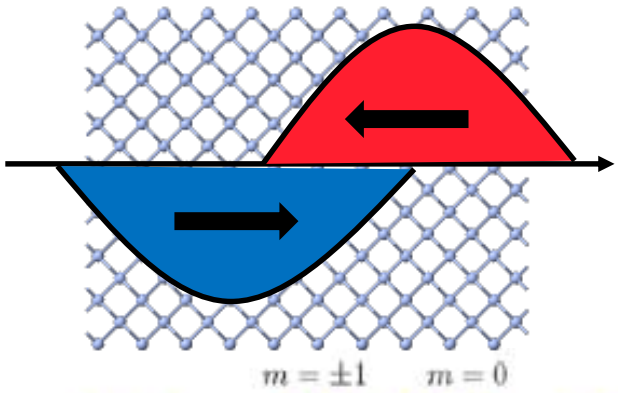
MOLECULAR SPINTRONICS

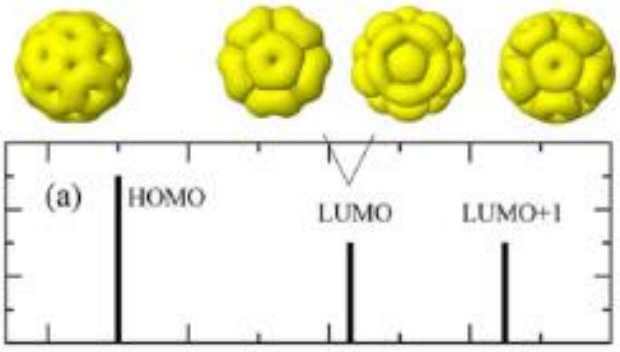


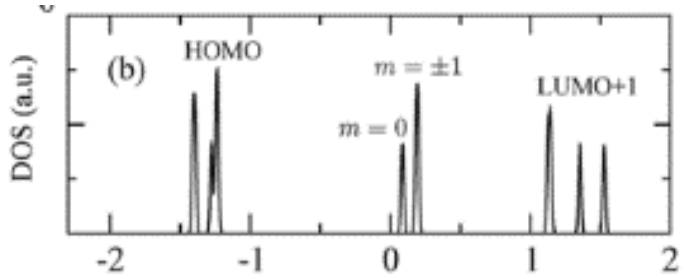
MOLECULAR SPINTRONICS

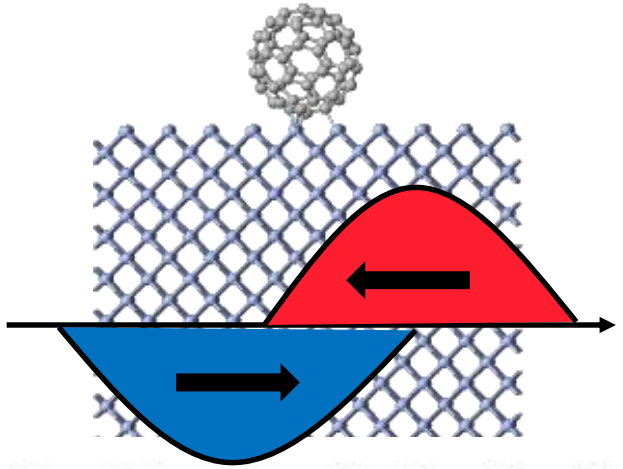


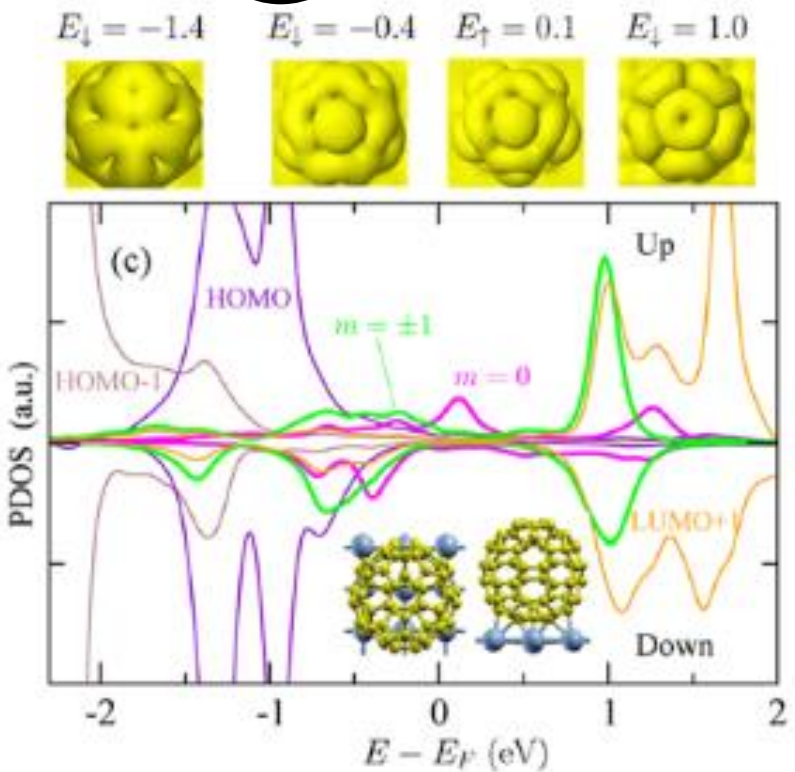
SPINTERFACE AND ORBITAL MATCHING











OUTLINE

- Tunnelling magnetoresistance: C_{60}/Cr(001)
- Tuning magneto-crystalline anisotropy: C_{60}/Co
- Influence of substrate on switchable molecules

TUNELLING MAGNETORESISTANCE

Nano Lett. **12,** 4558-4563 (2012).

NANO LETTERS

Letter

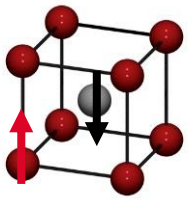
pubs.acs.org/NanoLett

Large Magnetoresistance through a Single Molecule due to a Spin-Split Hybridized Orbital

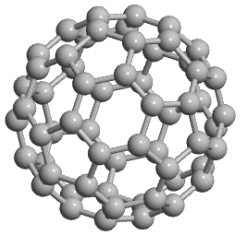
S. L. Kawahara,[†] J. Lagoute,*[,†] V. Repain,[†] C. Chacon,[†] Y. Girard,[†] S. Rousset,[†] A. Smogunov,[‡] and C. Barreteau[‡]

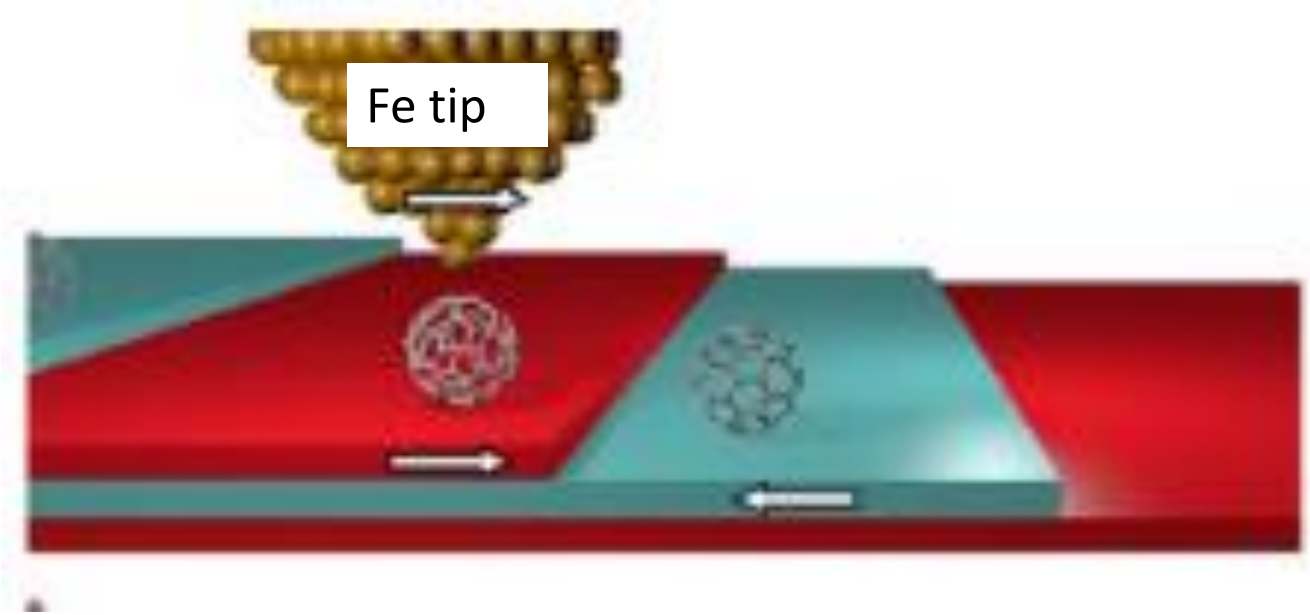
SYSTEM: C60/Cr(001)

Cr: AF material



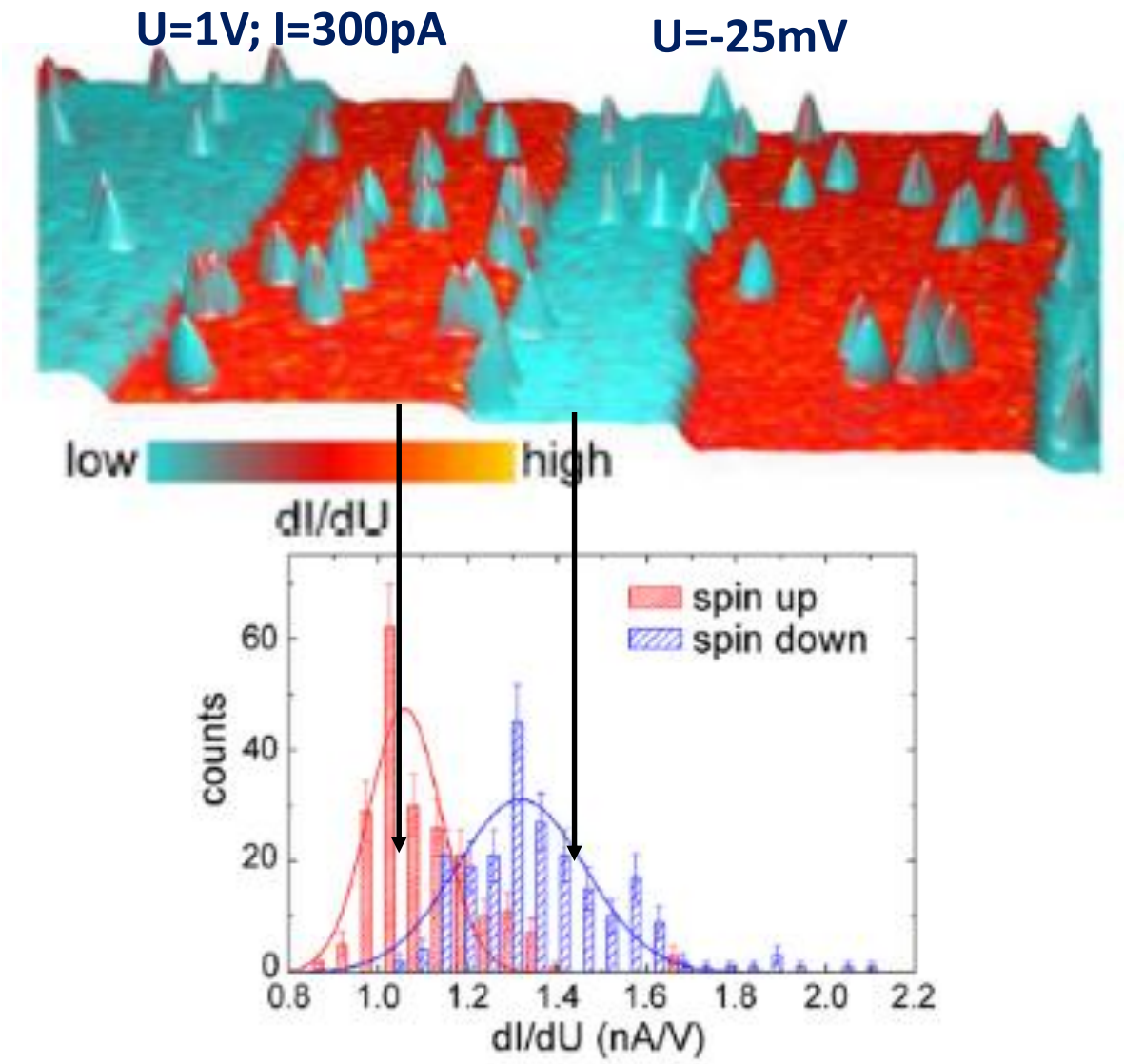
C_{60}





STM IMAGES: C60/Cr(001)

STM topograph + dI/dU map



MODELLING TOOL

DFT

Plane wave basis set

Ultra-soft pseudo-potentials

Many analyzing tools

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER
J. Phys.: Condens. Matter **21** (2009) 395502 (19pp) doi:10.1088/0953-8984/21/39/395502

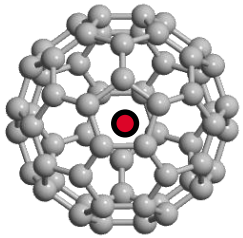
QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials

IOP Publishing Journal of Physics: Condensed Matter
J. Phys.: Condens. Matter **29** (2017) 465901 (30pp) https://doi.org/10.1088/1361-648X/aa8f79

Advanced capabilities for materials modelling with QUANTUM ESPRESSO

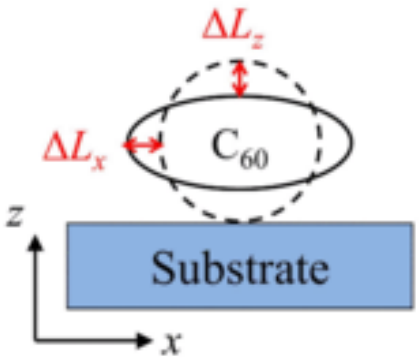
SPECTRUM OF ISOLATED C_{60}

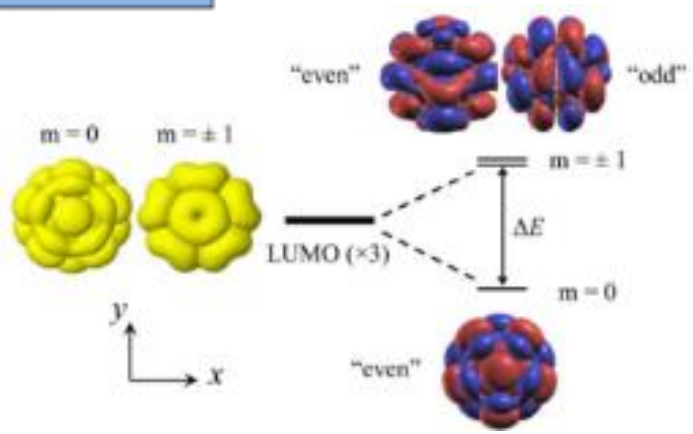
Pentagonal orientation

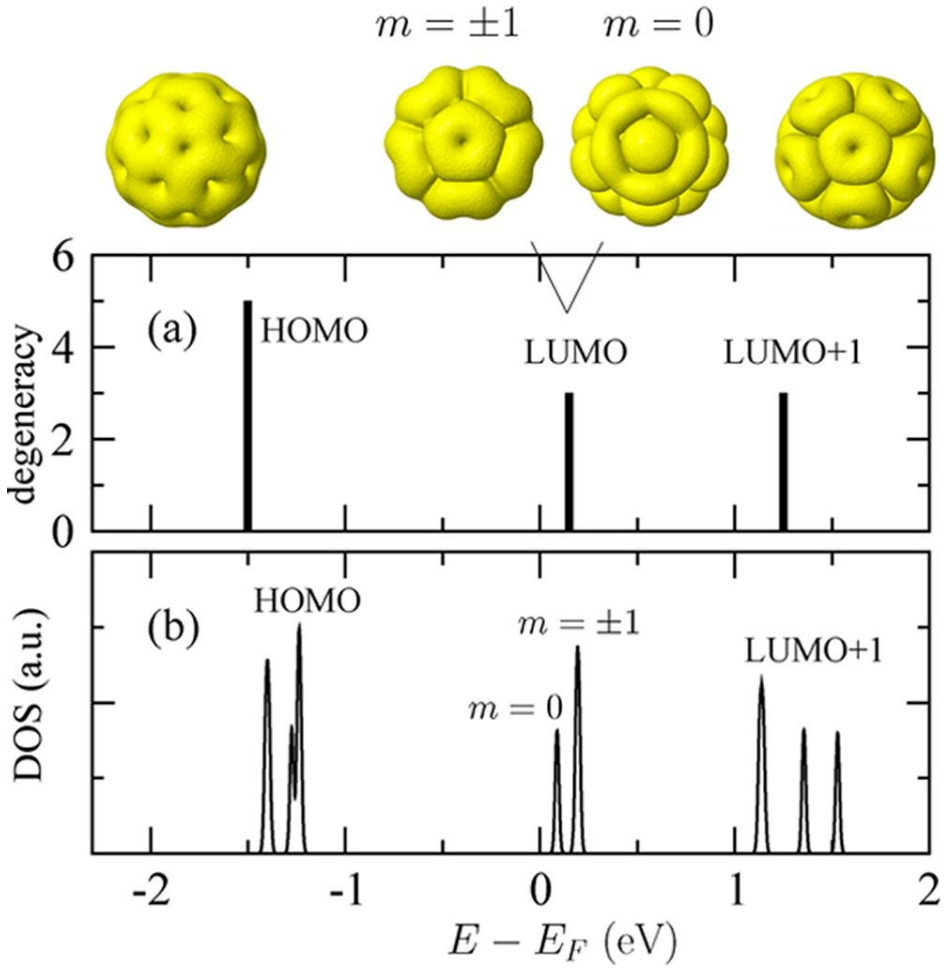


Isolated C_{60}

Distorted C_{60}

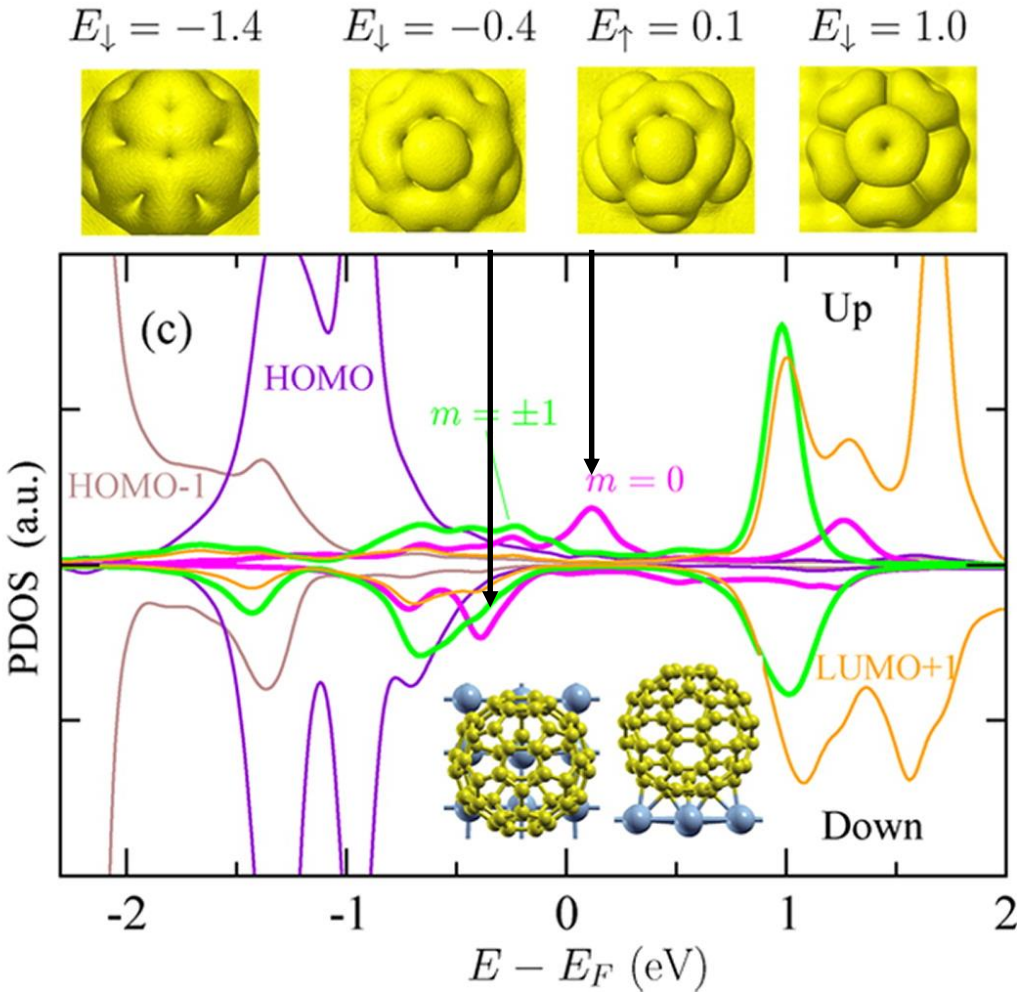






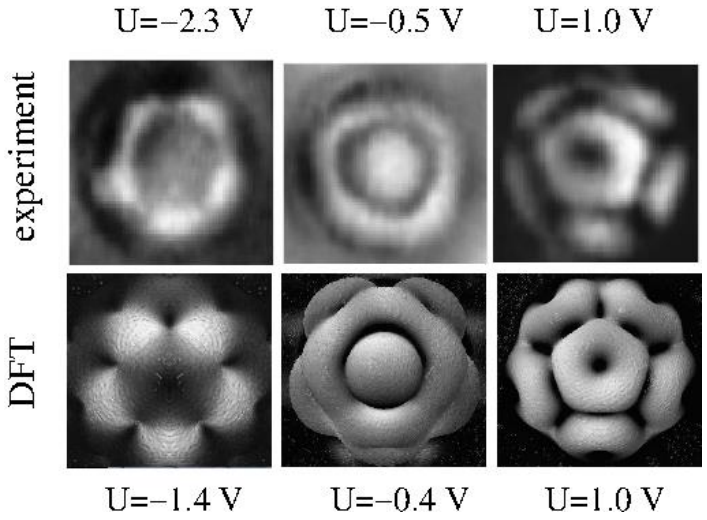
SPECTRUM OF C_{60}/Cr(001)

Molecular orbital projected DOS



$$I(r,U) \propto \int_{E_F}^{E_F+eU} n(r,E)dE$$

dI/dU map



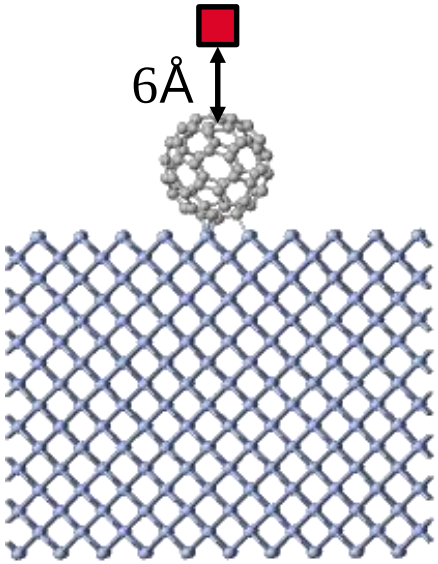
VACUUM DENSITY OF STATES

Tersoff-Hamann approximation

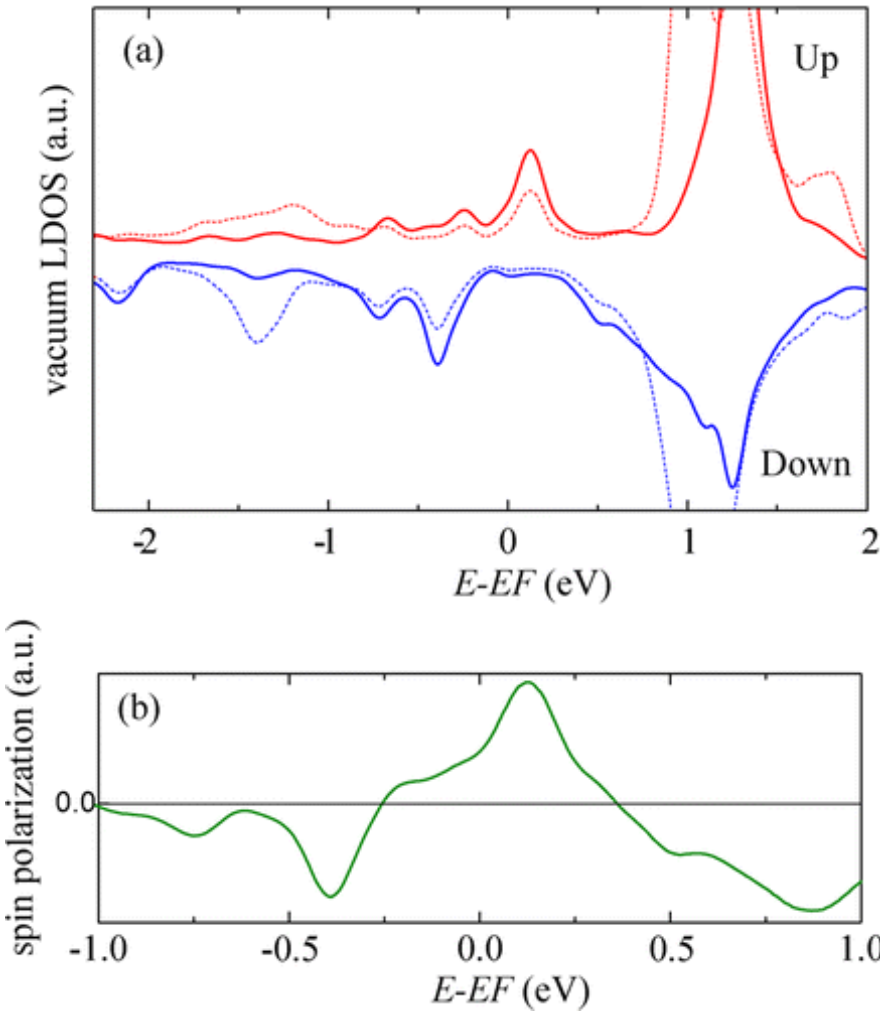
$$G = \frac{dI}{dU} \propto \sum_{\sigma} n_T^{\sigma} n_S^{\sigma} \left(R_T, E_F + eU \right)$$

$$n_S^{\sigma} \left(R_T, E_F + eU \right) = \sum_j \left| \psi_{Sj}^{\sigma} \right|^2 \delta(E_j - E_F - eU)$$

Fully polarized tip: $n_T^{\uparrow} = 0 \;\; n_T^{\downarrow} \neq 0$



Vacuum DOS



C_{60}/FERROMAGNETIC INTERFACES

Phys. Rev. B **93,** 085425 (2016).

PHYSICAL REVIEW B 93, 085425 (2016)

Symmetry-selected spin-split hybrid states in C_{60}/ferromagnetic interfaces

Dongzhe Li,[1] Cyrille Barreteau,[1,2] Seiji Leo Kawahara,[3] Jérôme Lagoute,[3] Cyril Chacon,[3] Yann Girard,[3] Sylvie Rousset,[3] Vincent Repain,[3] and Alexander Smogunov[1,*]

C60/ bcc Cr(001) , bcc Fe(001), bcc Co(001), fcc Co(001), hcp Co(0001)

Pentagonal symmetry is optimal for TMR

+

The surface symmetry and compacity is also crucial:
bcc(001) is optimal

ORBITAL MATCHING

TUNING MAGNETIC ANISOTROPY

PRL **114,** 247203 (2015).

PRL 114, 247203 (2015) PHYSICAL REVIEW LETTERS week ending 19 JUNE 2015

Tuning the Magnetic Anisotropy at a Molecule-Metal Interface

K. Bairagi,[1] A. Bellec,[1] V. Repain,[1,*] C. Chacon,[1] Y. Girard,[1] Y. Garreau,[1] J. Lagoute,[1] S. Rousset,[1] R. Breitwieser,[2] Yu-Cheng Hu,[2] Yen Cheng Chao,[2] Woei Wu Pai,[2,4] D. Li,[3] A. Smogunov,[3] and C. Barreteau[3,5]

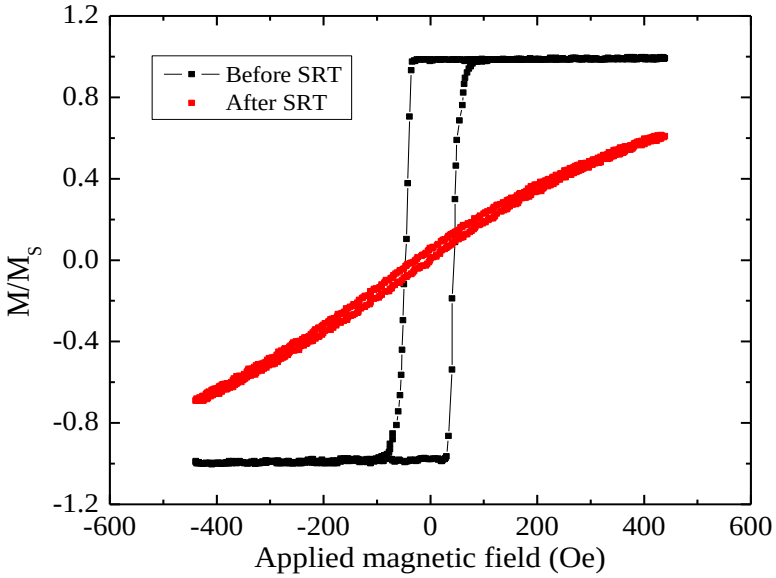
Co/Au(111) SUBSTRATE

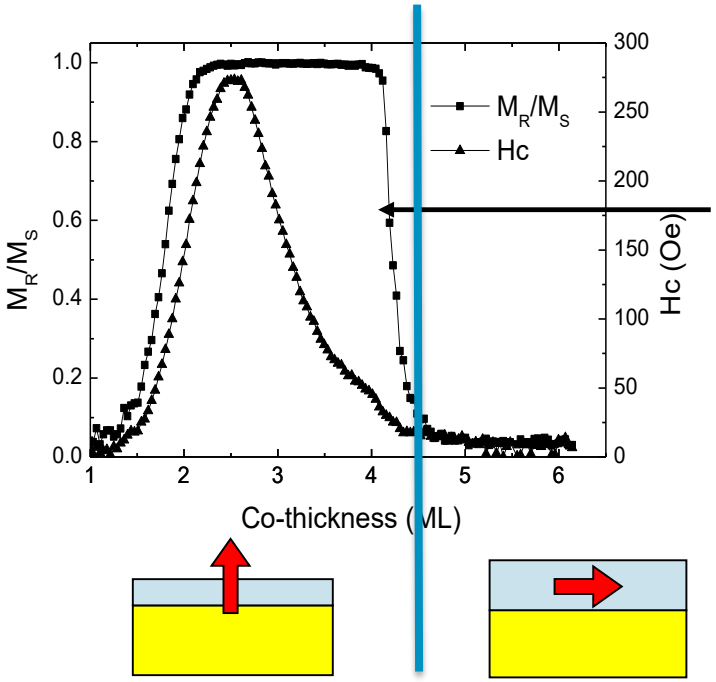
Spin Reorientation Transition (SRT) at t*=4.2 ML

$$K^{eff} = \frac{E^{MCA} + E^{shape}}{V} = K^{v} + \frac{K^{s}}{t}$$

Co/Au(111) K^{s}= 0.75 mJ.m^{-2} and K^{v}= -900 kJ.m^{-3}

Polar MOKE



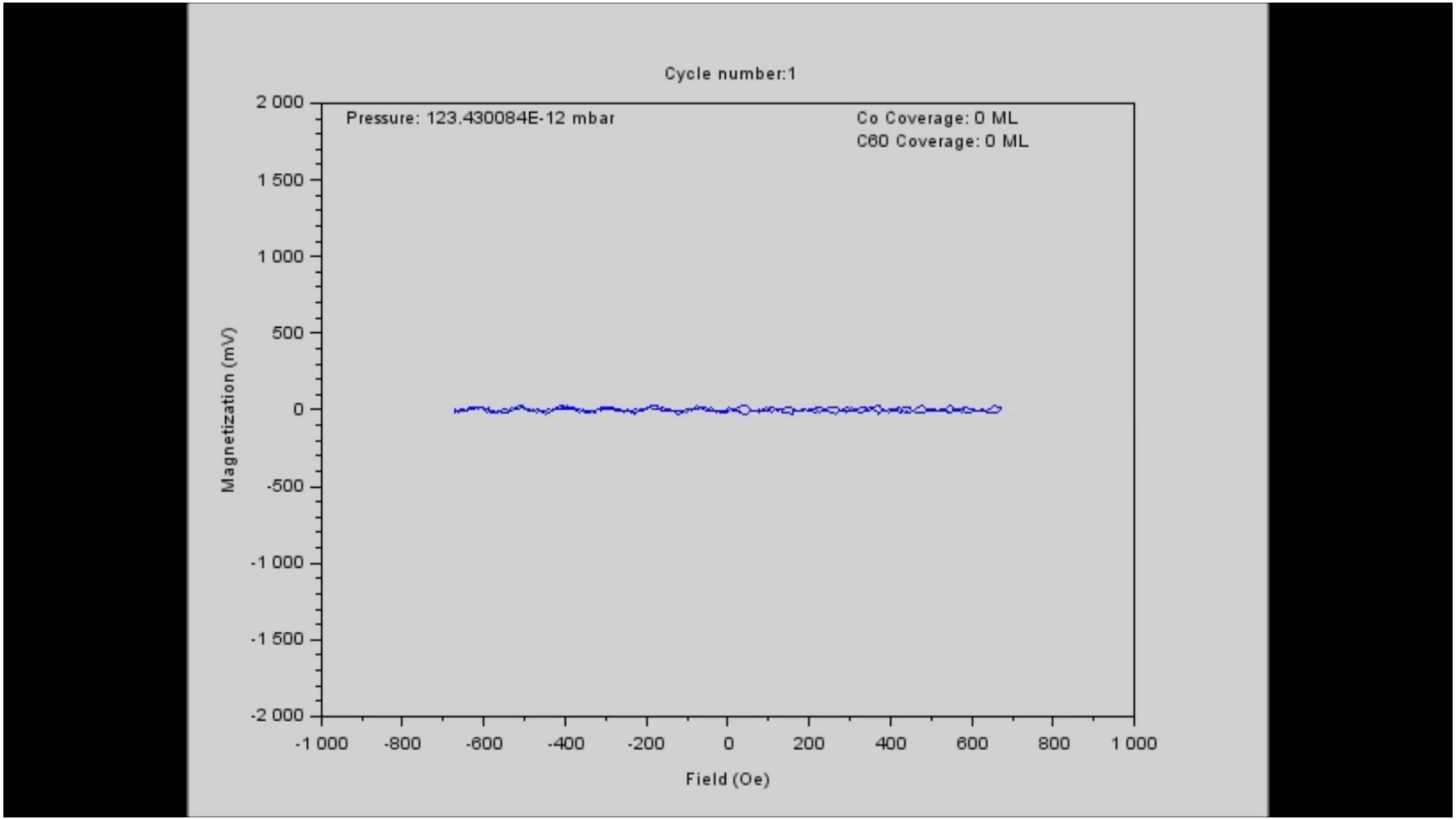


SRT

Ultra sensitive to magnetic anisotropy change close to the SRT

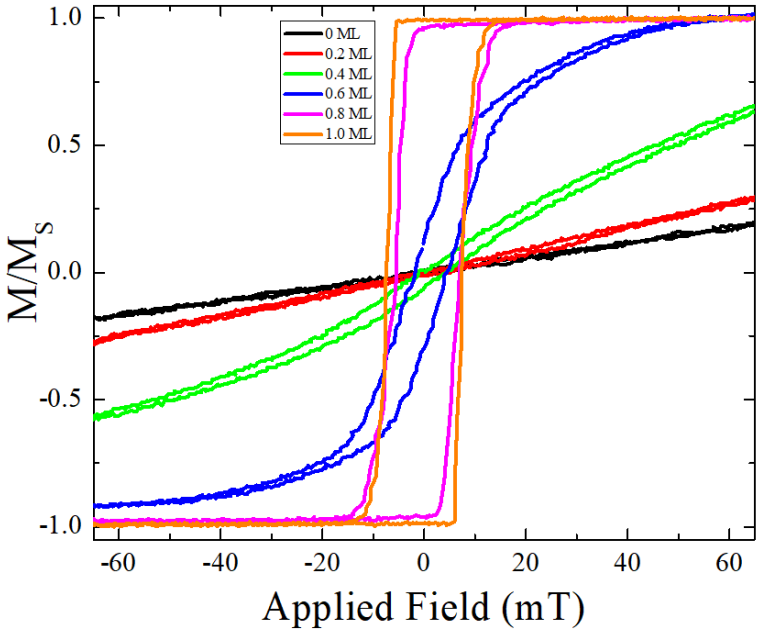
C60/Co/Au(111) EXPERIMENT

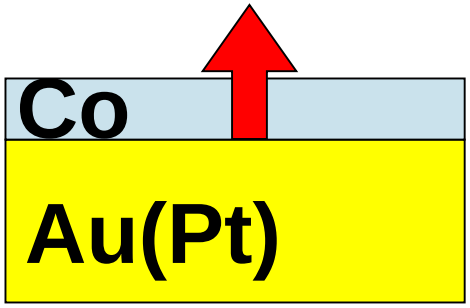
- Adsorption of C_{60} on Co(0001)/Au(111)

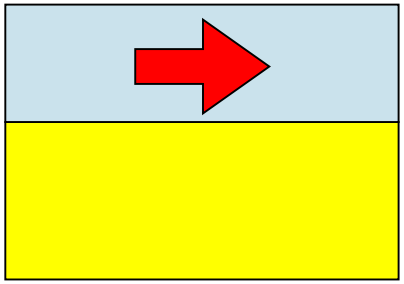


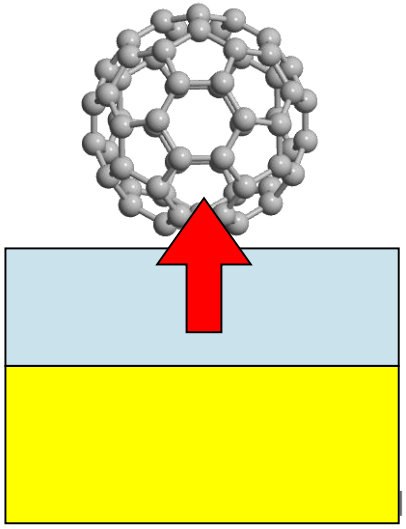
C60/Co/Au(111) EXPERIMENT

C60 **favors** « out-of-plane » magnetization





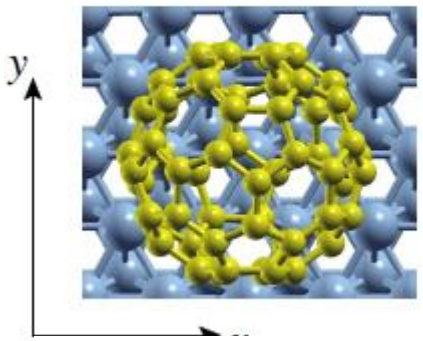


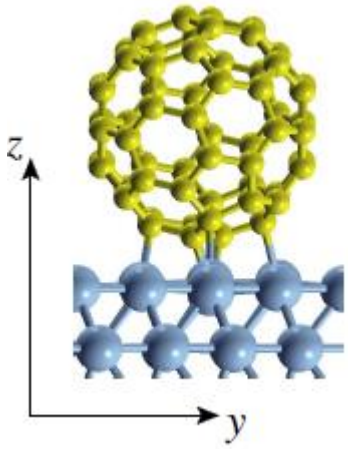


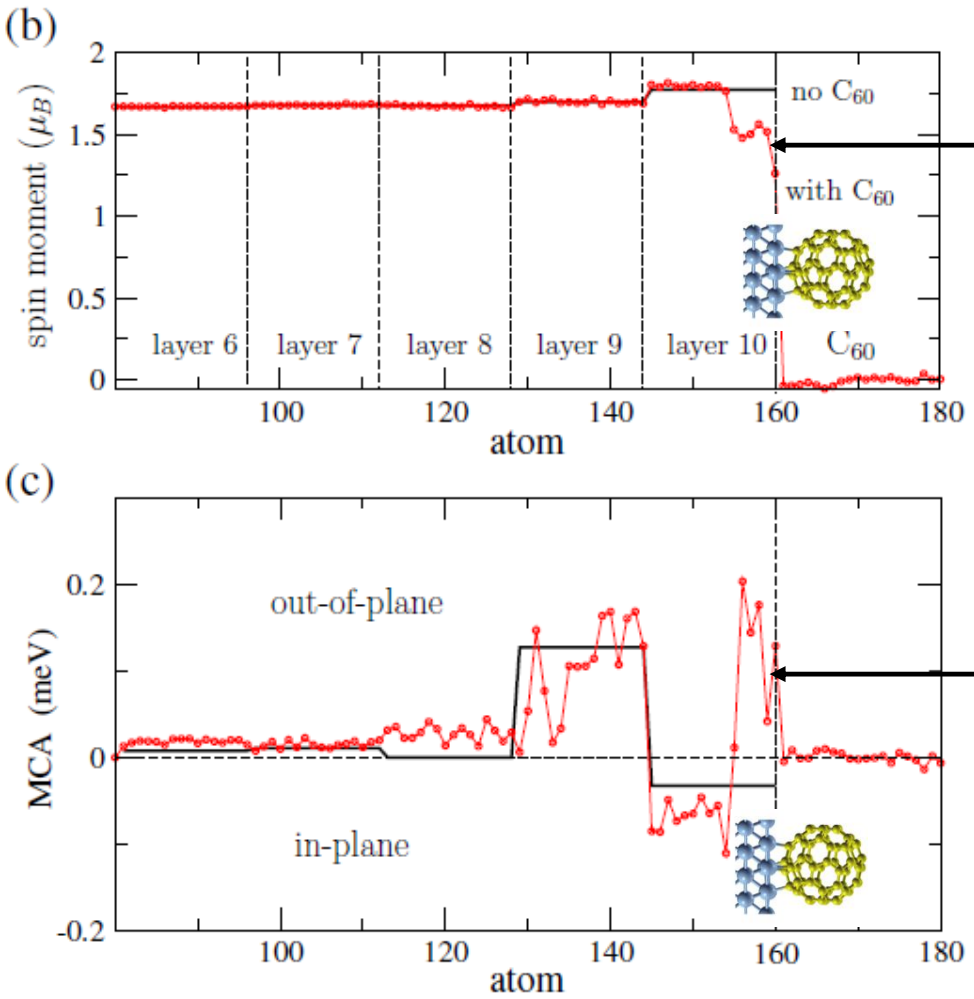
C60/Co MODELLING

•Adsorption of C_{60} on Co(0001)/Au(111): Theory

DFT calculation:
C60/10L Co (4x4)







Decrease of magnetization

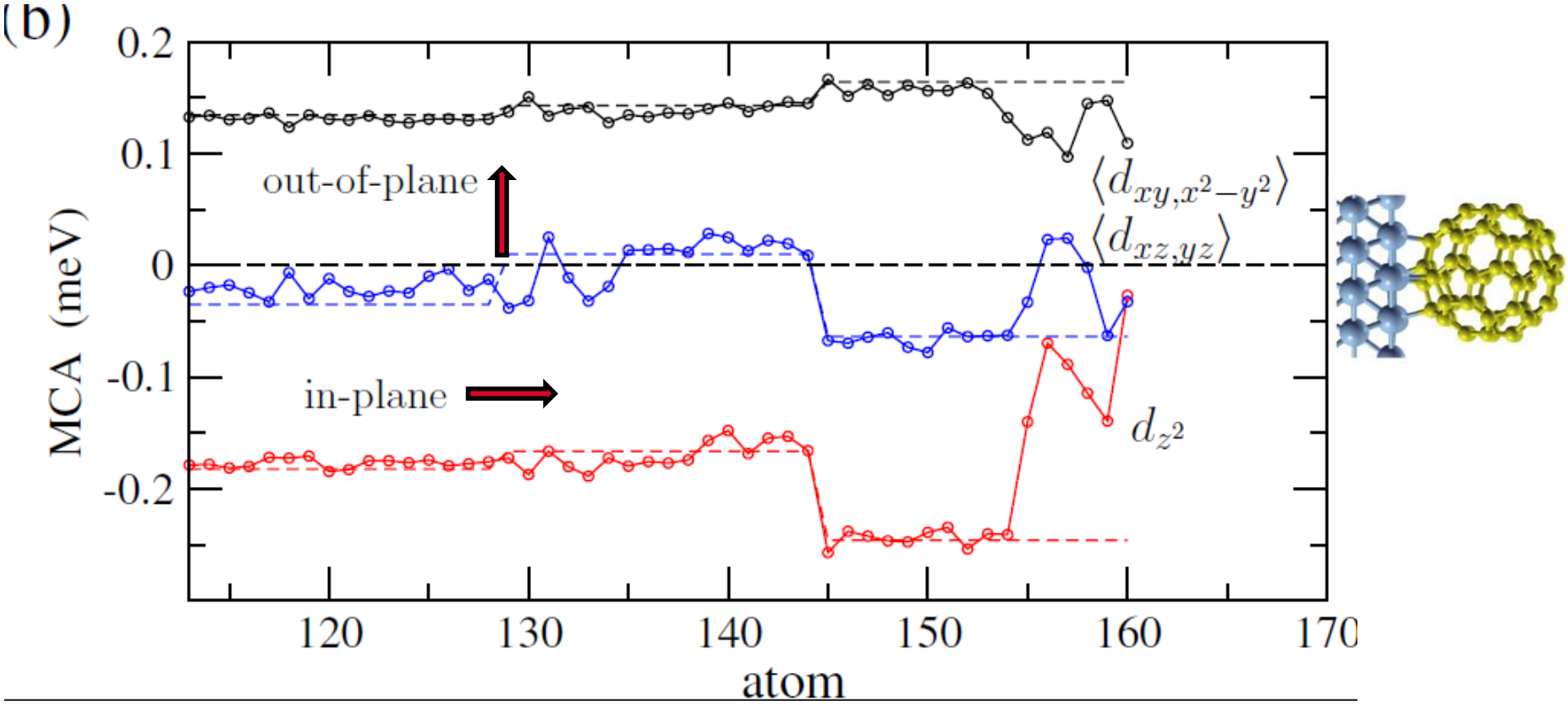
increase of "out-of-plane" MCA

$$\Delta E^{ani} = \underbrace{\Delta E^{MCA}}_{0.9} + \underbrace{\Delta E^{shape}}_{0.6} = 1.5meV$$

For 5x16 Co atoms $\Delta E^{ani} = 19\mu eV / atom$

ORBITAL ANALYSIS

Orbital-resolved MCA

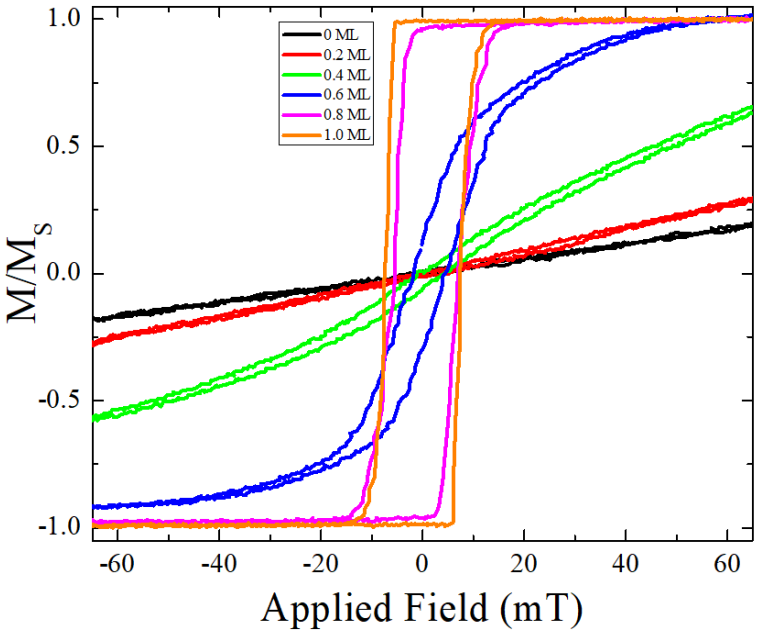


Experiment: C60 favors « out-of-plane » magnetization

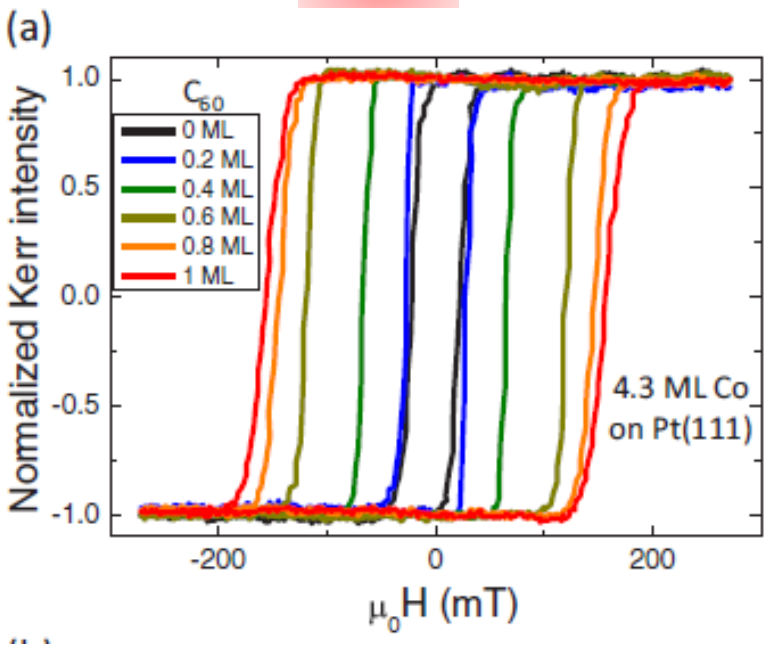
Theory: C60 kills « in-plane » dz^2 component of MCA

C_{60}/Co/Au(111) VERSUS C_{60}/Co/Pt(111) EXPERIMENT

Co/Au



Co/Pt



Increase of coercive field

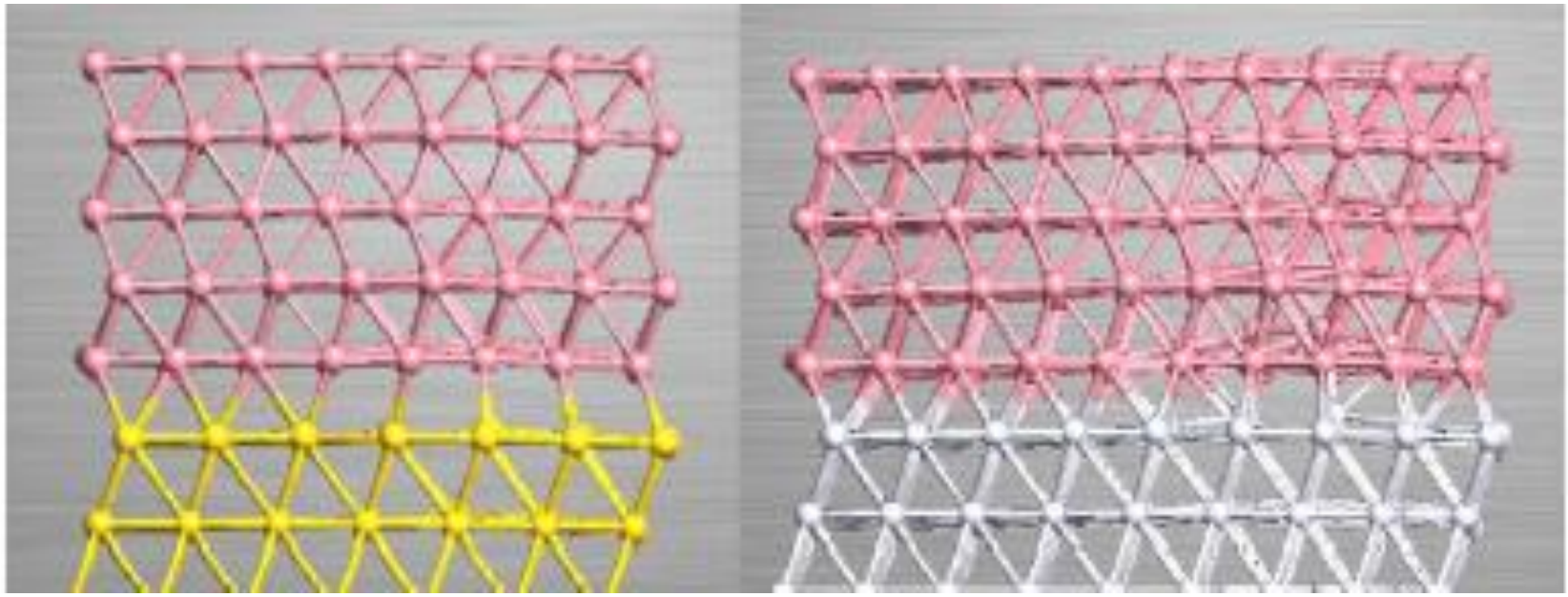
100% for C_{60}/Co/Au
700% for C_{60}/Co/Pt

PRB **98,** 085432 (2018)

Co/Au(111) VERSUS Co/Pt(111)

Co/Au(111)

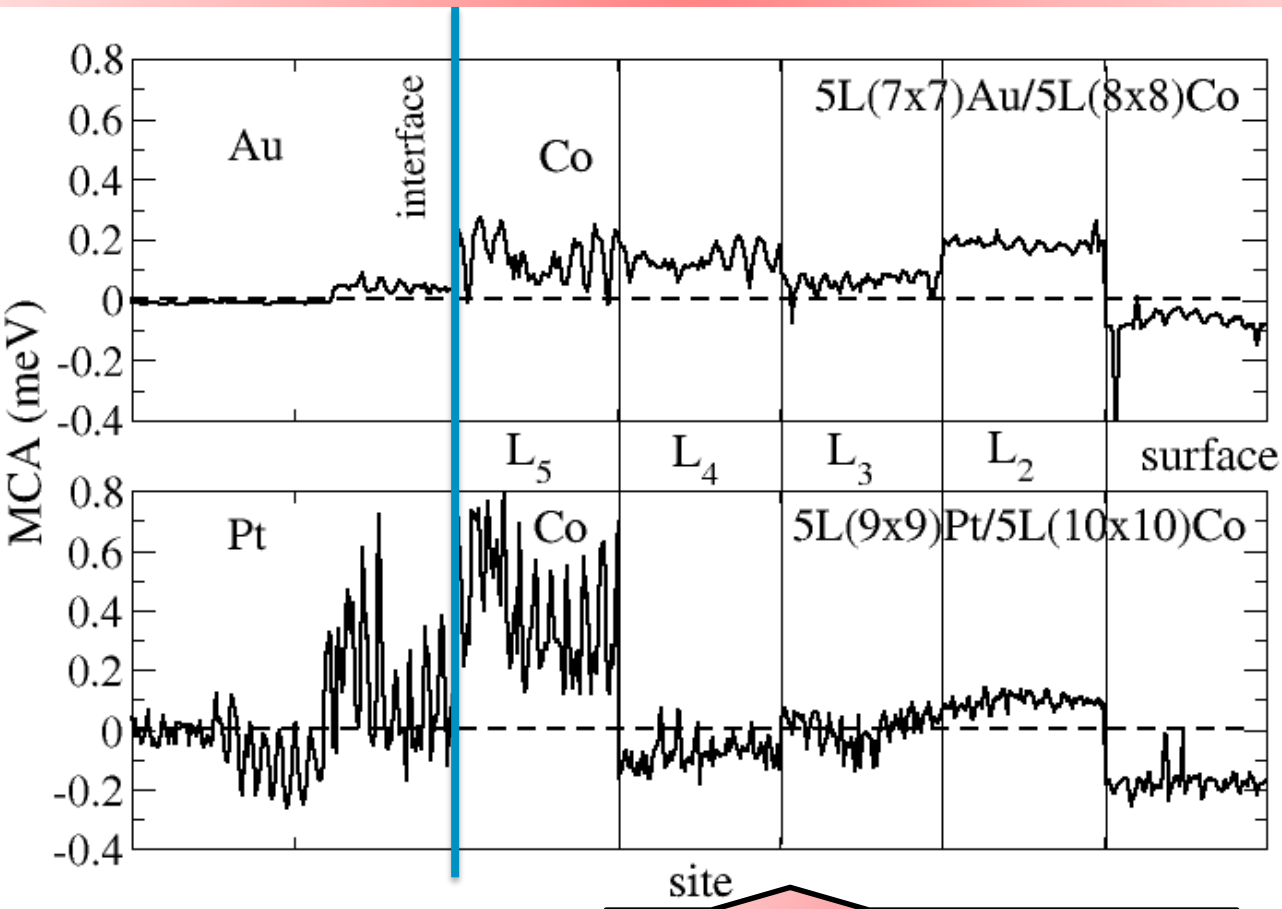
Co/Pt(111)



residual strain

Co/Au(111) VERSUS Co/Pt(111)

strain induced by interface can affect the surface MCA



STRAINTRONICS

INFLUENCE OF SUBSTRATE ON SWITCHABLE MOLECULES

Nature Comm. **7,** 12212 (2016). + submitted….

ARTICLE

Received 20 Jan 2016 | Accepted 13 Jun 2016 | Published 18 Jul 2016

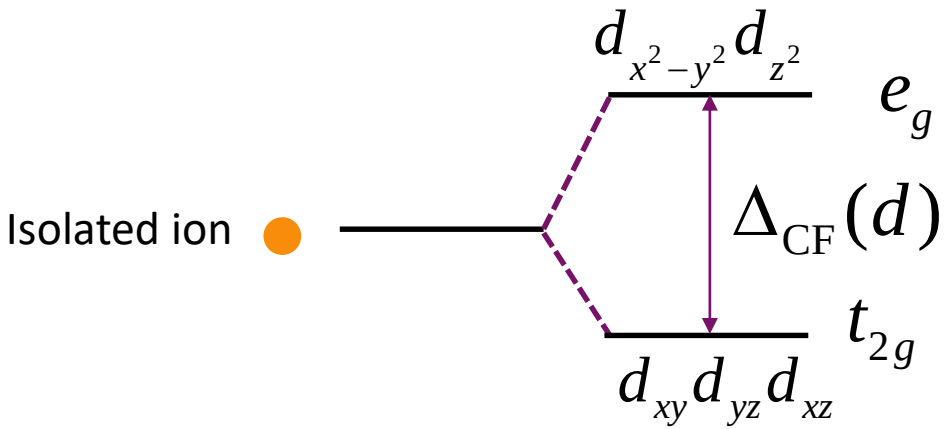
DOI: 10.1038/ncomms12212 OPEN

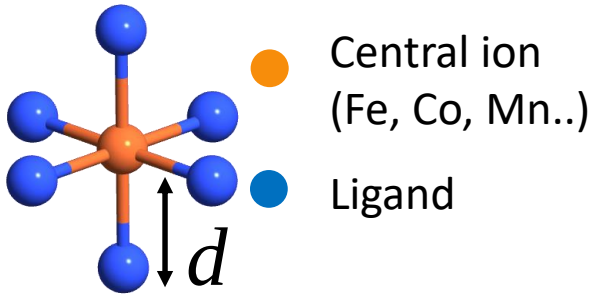
Molecular-scale dynamics of light-induced spin cross-over in a two-dimensional layer

Kaushik Bairagi[1], Olga Iasco[2], Amandine Bellec[1], Alexey Kartsev[3,4], Dongzhe Li[3], Jérôme Lagoute[1], Cyril Chacon[1], Yann Girard[1], Sylvie Rousset[1], Frédéric Miserque[5], Yannick J. Dappe[3], Alexander Smogunov[3], Cyrille Barreteau[3], Marie-Laure Boillot[2], Talal Mallah[2] & Vincent Repain[1]

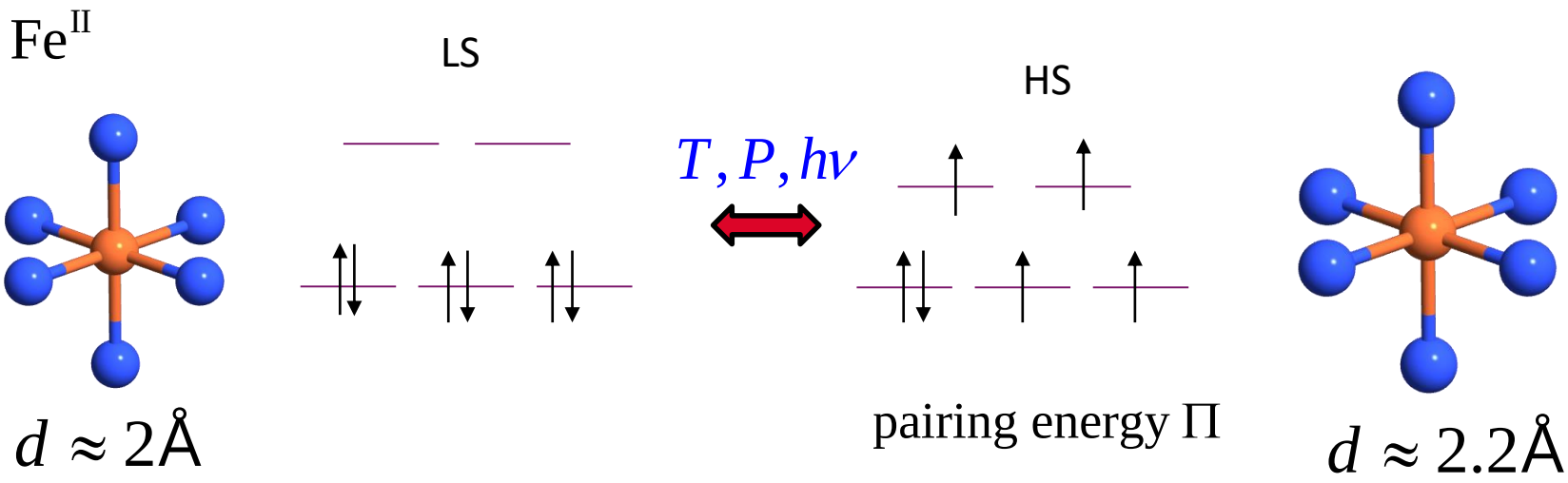
SPIN CROSSOVER MOLECULES

Ion in octahedral « cage »





LS-HS switching



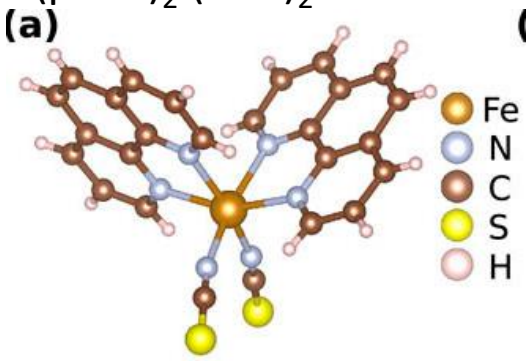
SCO ON SURFACE

Interaction with surface can greatly affect the SCO

Freezing of the configuration

Nature Comm. **3,** 938 (2012).

$Fe(phen)_2 (NCS)_2$

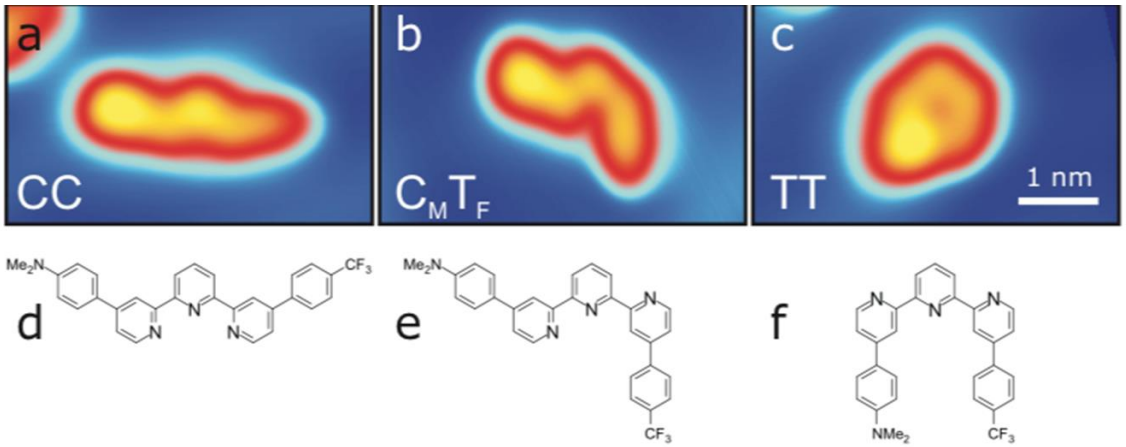


On Cu(001) → **no switching**

On CuN/Cu(001) → **switching (with voltage)**

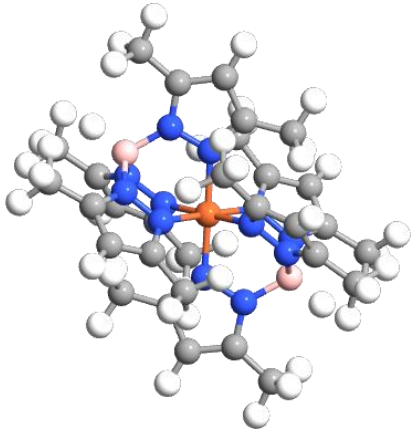
fragmentation

Gruber et al.



terpyridine-based spin-crossover complexes on Au(111)

$Fe^{II}[((CH3)_2Pz)_3BH]_2$



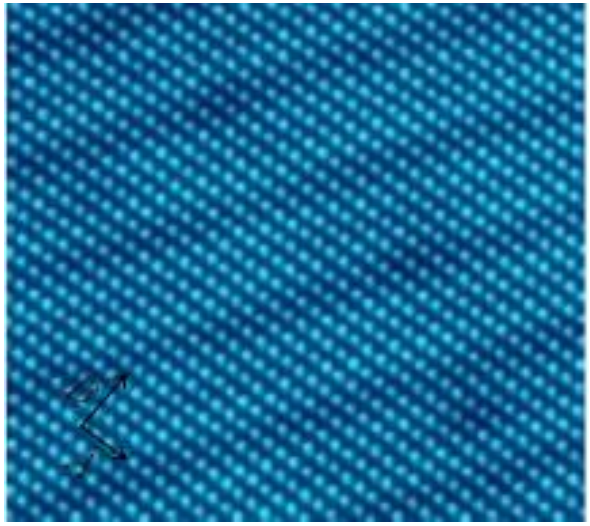
Bulk phase

- Complete spin transition with T → **ΔE=0.1eV**
- Structural bulk characterization

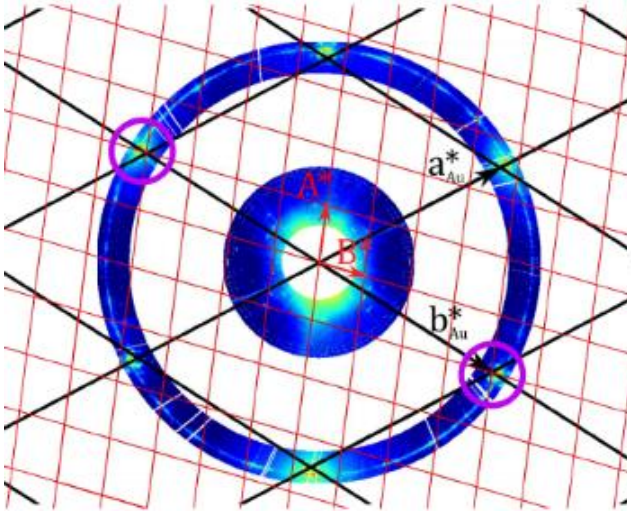
Journal of material chemistry C 42, 11067

2D self-assembly on Au(111)

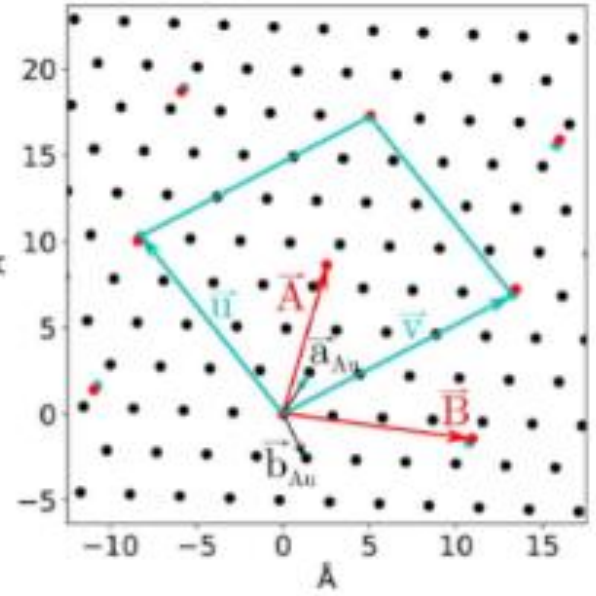
Real space (STM)



Reciprocal space (GIXD)

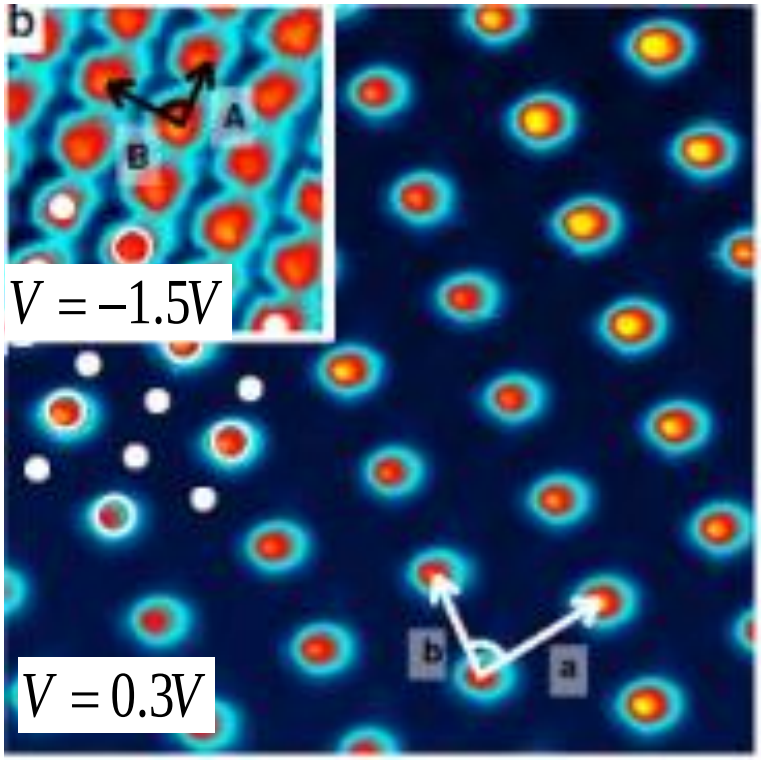


Epitaxial structure



MIXED LS AND HS PHASE

3x1 structure

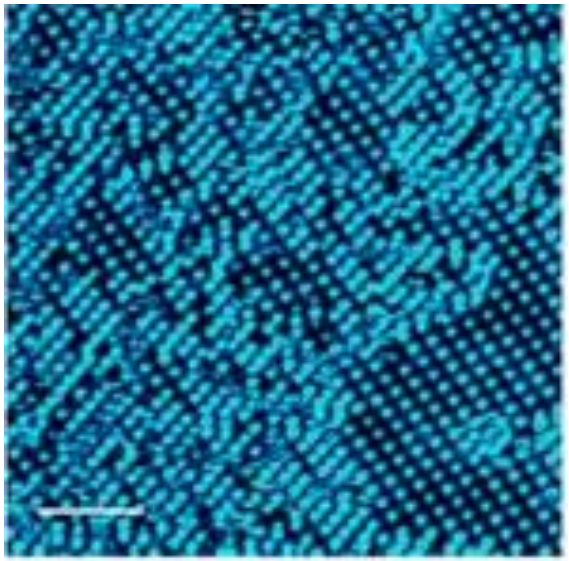


Nature Comm. **7**, 12212 (2016).

- 1/3 of molecule are bright at 0.3V

Mixed LS-HS phase

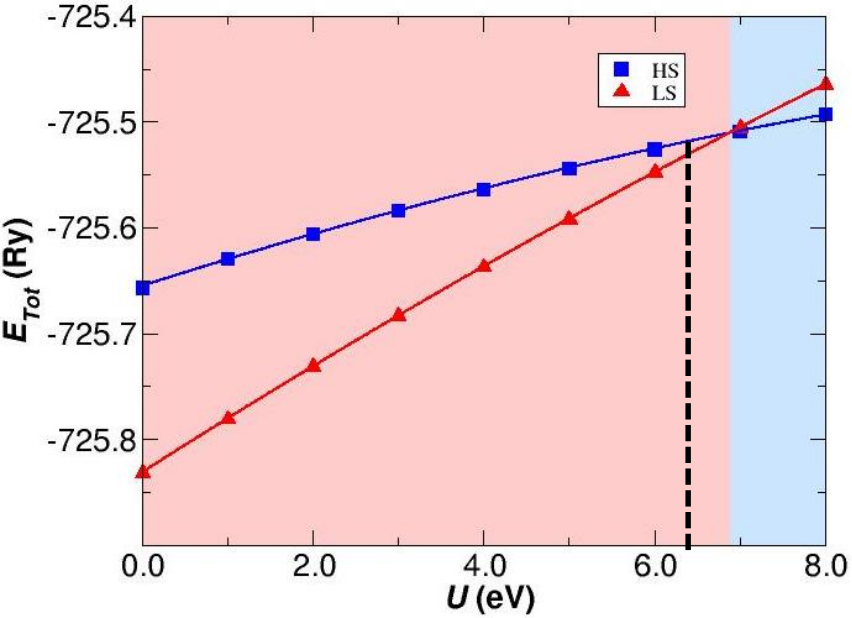
Switching under blue illumination…



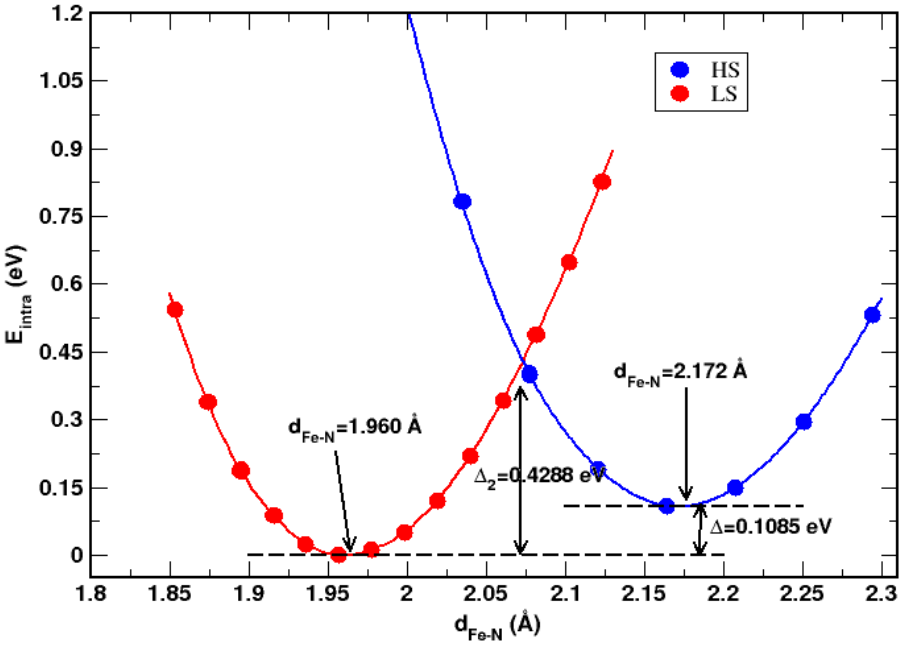
DFT MODELLING OF ISOLATED SCO

Standard DFT not sufficient → DFT+U

Tuning U in DFT+U



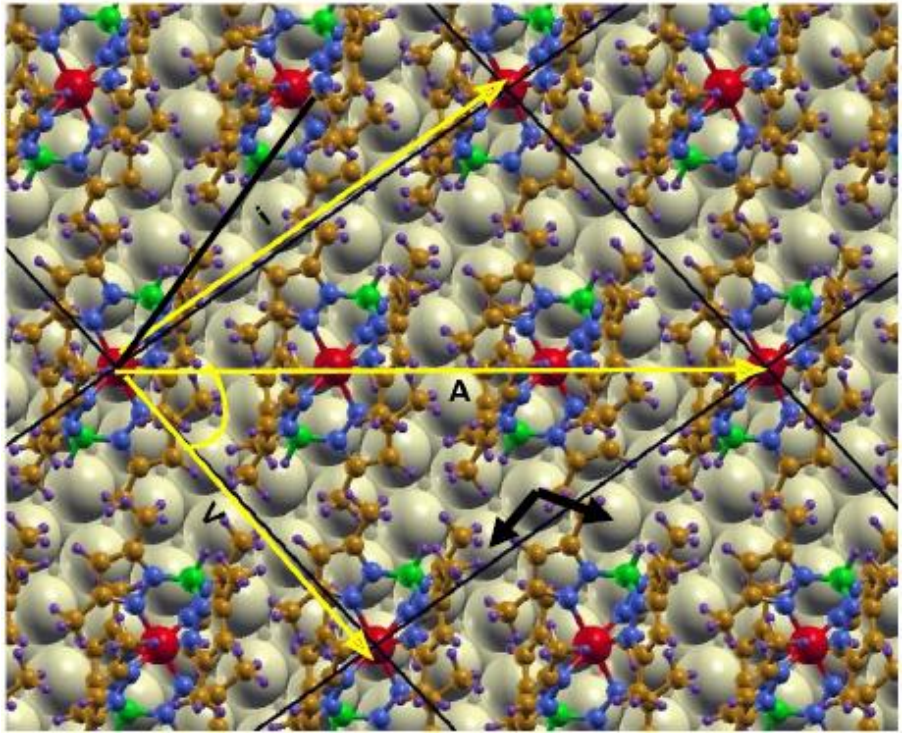
From LS to HS



$$\Delta = E_{\mathrm{HS}} - E_{\mathrm{LS}} = 0.1eV$$

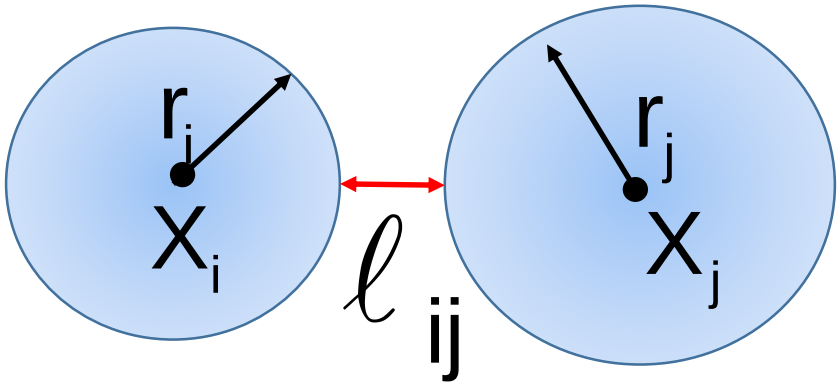
DFT MODELLING SCO/SURFACE

3x1 SCO / 3 Au(111) layers



Spin configuration	LS-HS-HS	LS-HS-LS	LS-LS-LS	HS-HS-HS
Energy (meV)	0	2.3	28.1	15.0

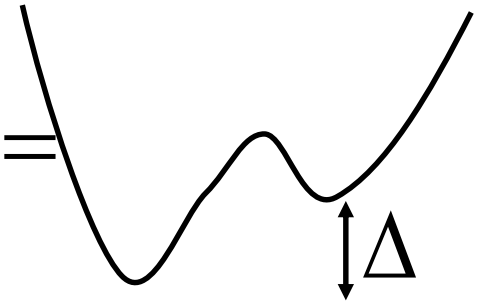
TOWARDS A GENERIC MODEL



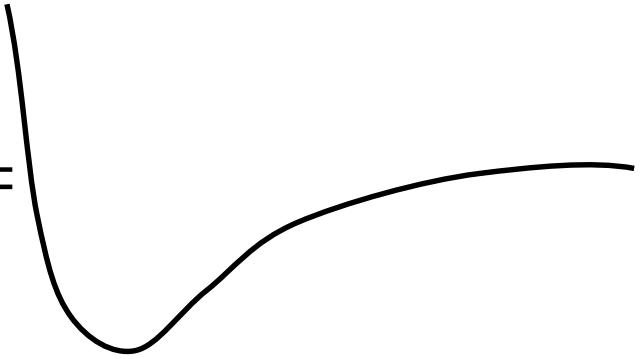
$$\ell_{ij} = \underbrace{\left|X_i - X_j\right|}_{x_{ij}} - r_i - r_j$$

$$r = d_{Fe-N} + \delta$$

$$E_{intra}(r) =$$

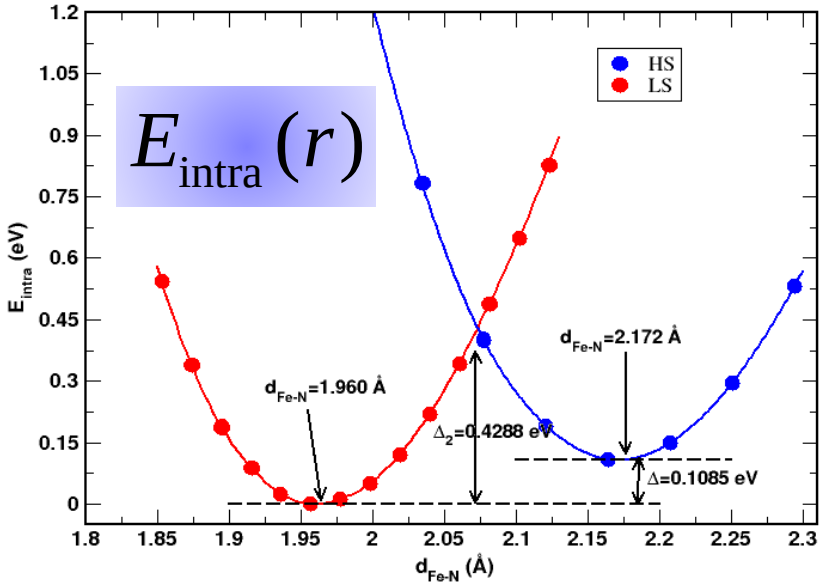


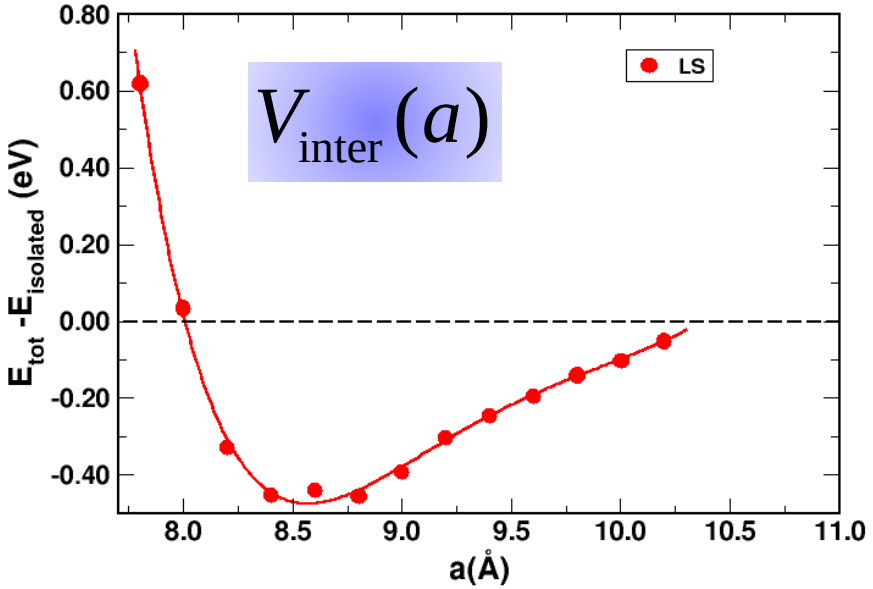
$$V_{inter}(\ell) =$$



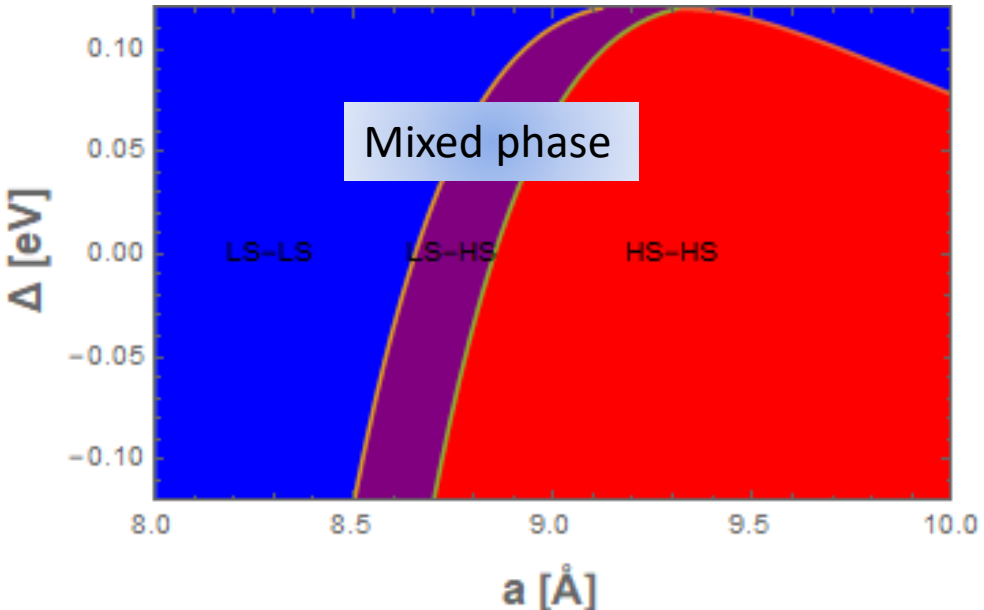
$$E_{tot}(\{X_i, r_i\}) = \sum_i E_{intra}(r_i) + \frac{1}{2}\sum_{\langle i,j\rangle} V_{inter}(X_{ij} - r_i - r_j)$$

MODEL OF A SCO CHAIN





Phase diagram



CONCLUSIONS PERSPECTIVES

CONCLUSION & PERSPECTIVES

- Spinterface: affects the molecule as well as the substrate
- Even rather low surface/molecule interaction can affect the intrinsic properties of the molecules
- Orbital matching: a combination between surface and molecule

Open perspectives based on **Orbital Engineering**

Room for rational design..

FINANCING

ANR, SPIROU

SPIn **R**esistance **O**n **U**ltimate molecular devices

FET open Grant No. 766726

COncepts and tool**S** in **M**olecular spintron**ICS**

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THANK YOU FOR YOUR ATTENTION

QUESTIONS?

COMMENTS?