WARWICK

The Beauty of Imperfection
(and it’s x-ray spectroscopic signatures)

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maurer group

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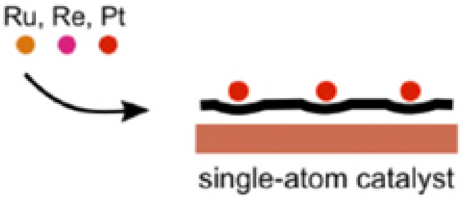
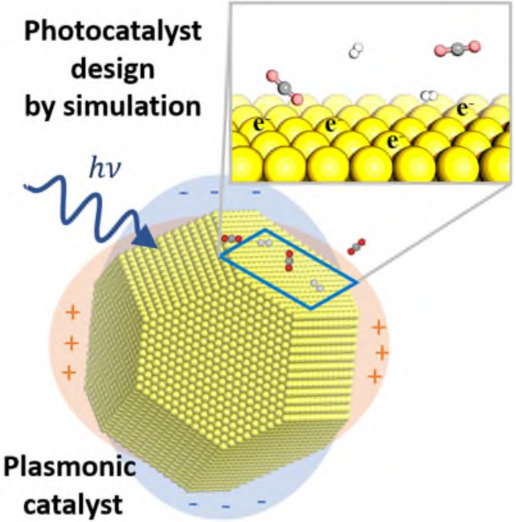
Recent Advances in Computer-aided X-ray Spectroscopy
RACXS 2024
17-20 June
Aalto University
Finland

Computational Surface Science

Design of functional nanostructures





Sam Hall (now HZB, Germany)

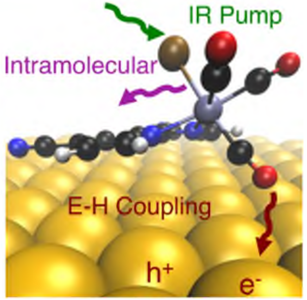
Benedikt Klein (now KBSI, Korea)

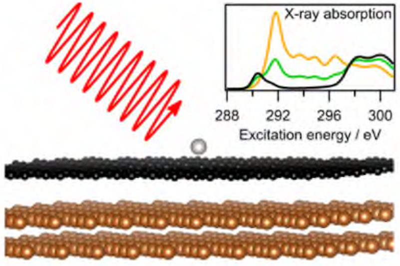
David Duncan (Diamond/ Nottingham)

Michael Gottfried (U Marburg)

Alex Saywell (Nottingham)

Ultrafast energy transfer & surface spectroscopy





LEVERHULME TRUST

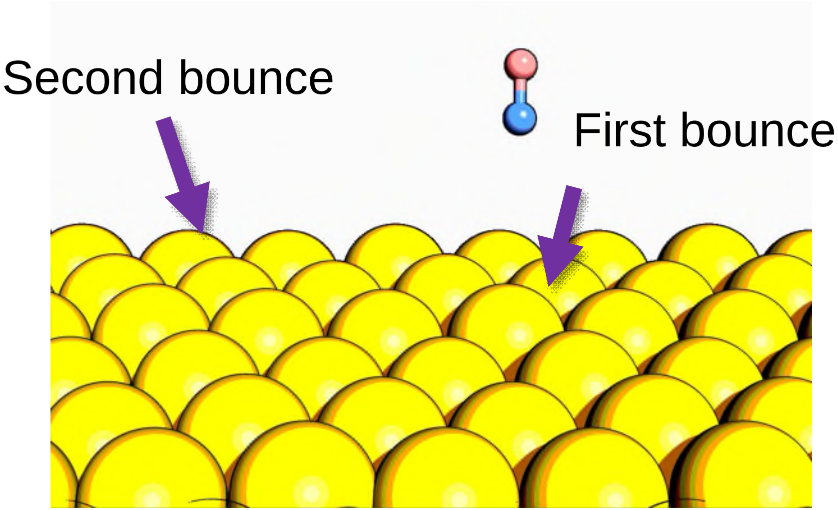
UK Research and Innovation

diamond

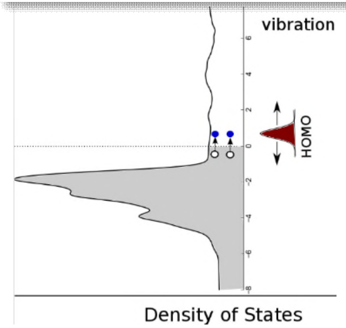
Measuring signatures of surface chemistry I

Throwing things at surfaces

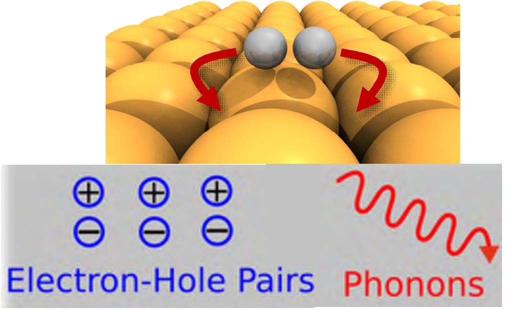
Final v_f, J_f, E_f Initial v_i, J_i, E_i



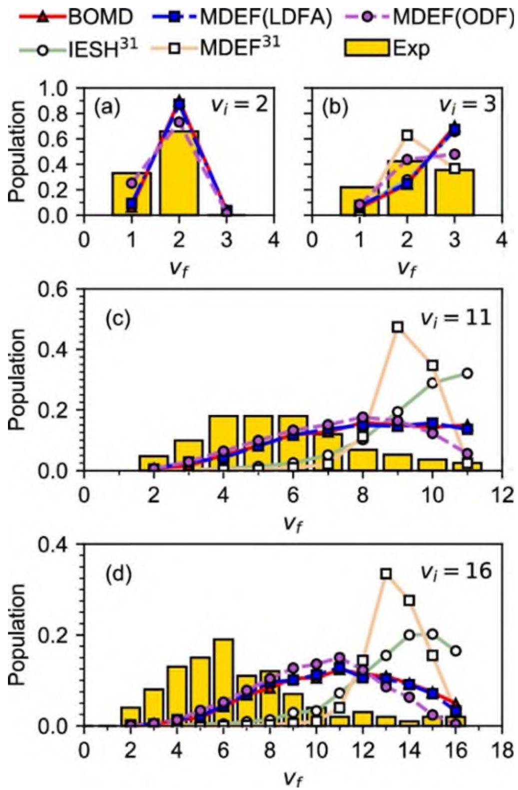
Electronic structure

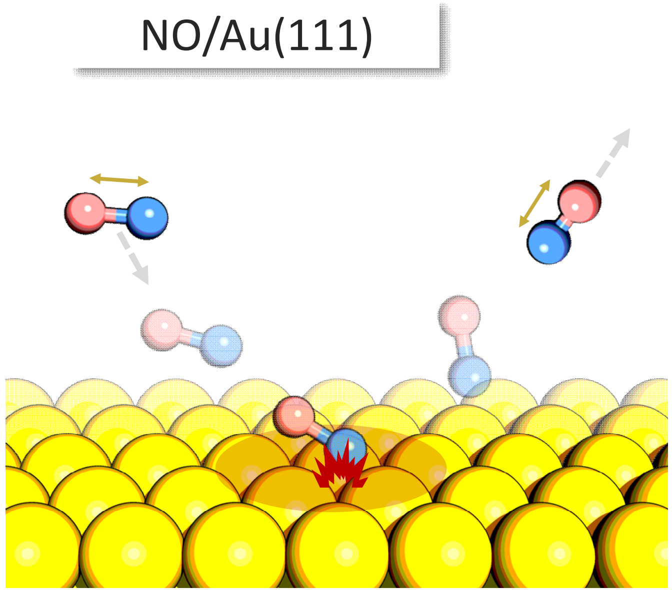


Energy dissipation



Direct simulation of quantum state-to-state scattering





Box et al., JACS Au 1, 164-173 (2021)

Nonadiabatic effects lead to energy dissipation into "Hot Electrons"

Molecular Beam Scattering experiments:

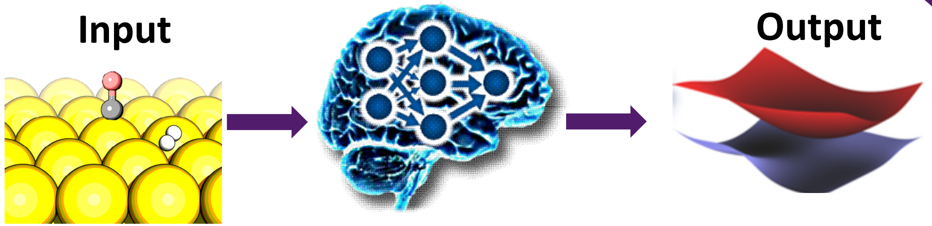
Huang, Rettner, Auerbach, Wodtke, Science 290, 111-114 (2000); Int. Rev. Phys. Chem. 23 513 (2004)

Our computational approach

FHI-aims
The ab initio materials simulation package

Electronic Structure Theory

Machine Learning of Electronic Structure



Develop machine learning surrogate models of electronic structure

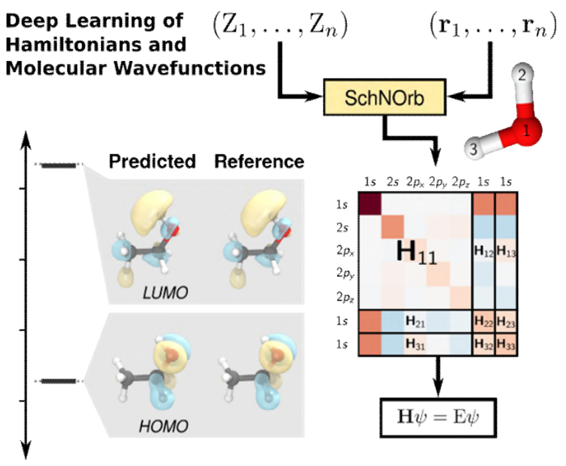
Coupling of Light and Electrons

Nonadiabatic Molecular Dynamics

DFTB

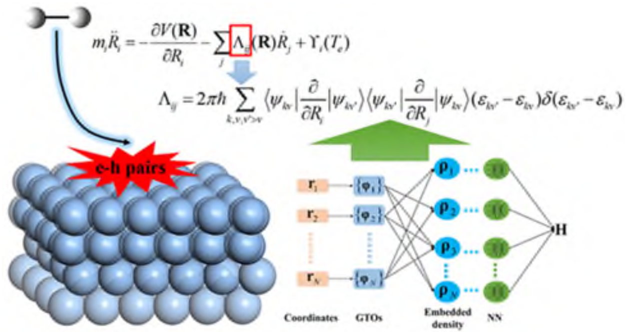
NQCDynamics.jl

Machine Learning of Electronic Structure



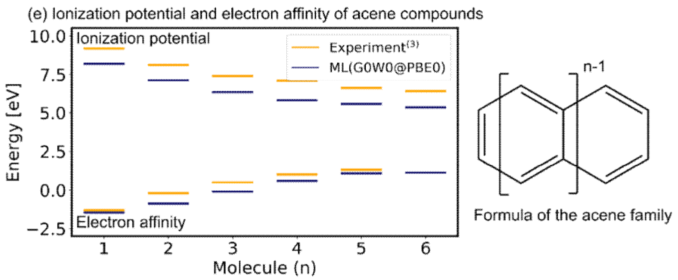
Nature Commun 10, 5024 (2019)

Machine Learning of nonadiabatic response



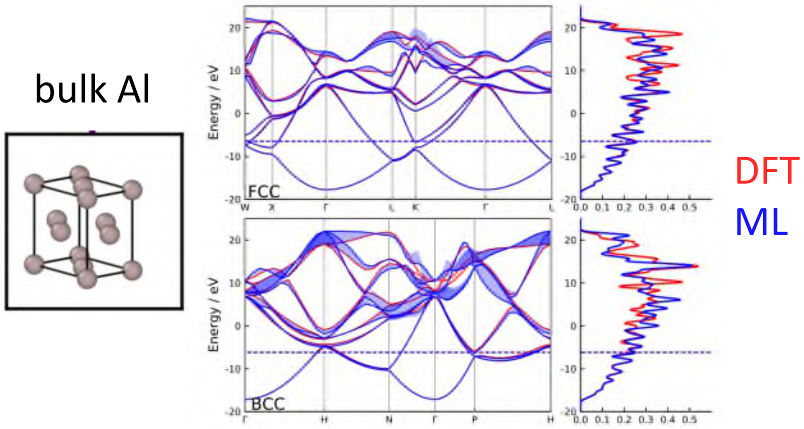
J. Phys. Chem. C 124, 186–195 (2020)

Deep learning of molecular spectroscopy



Chem. Sci. 12, 10755-10764 (2021)

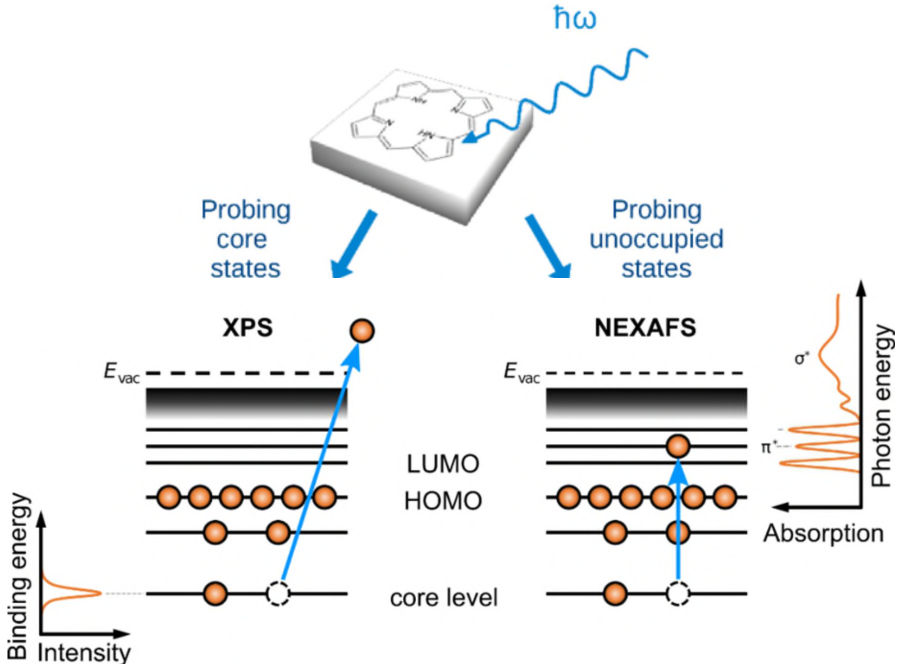
Machine learning of materials electronic structure



npj Computational Materials (2022)

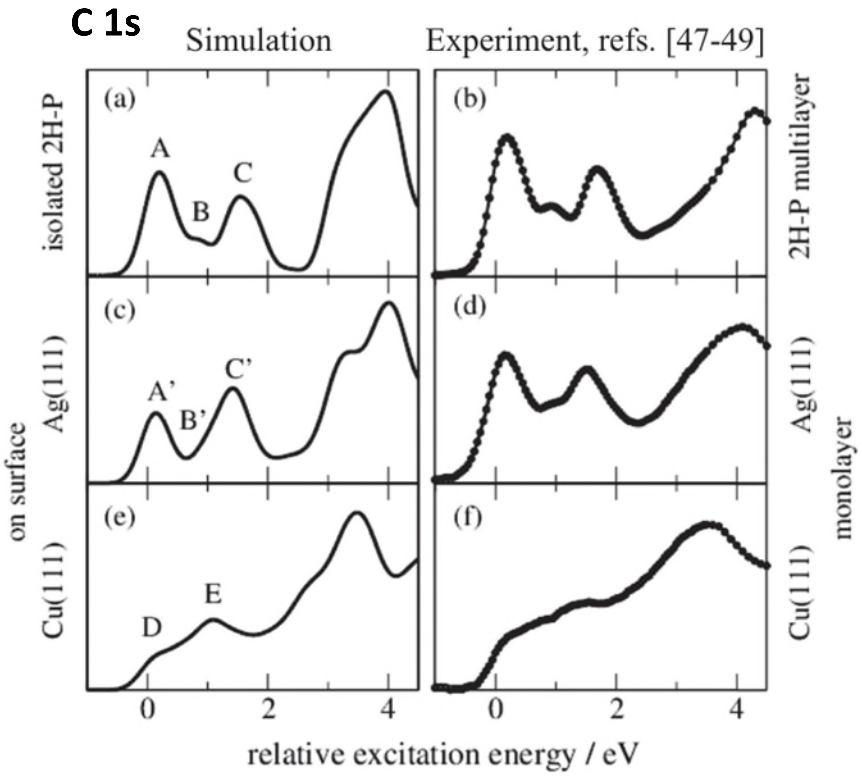
Measuring signatures of surface chemistry II

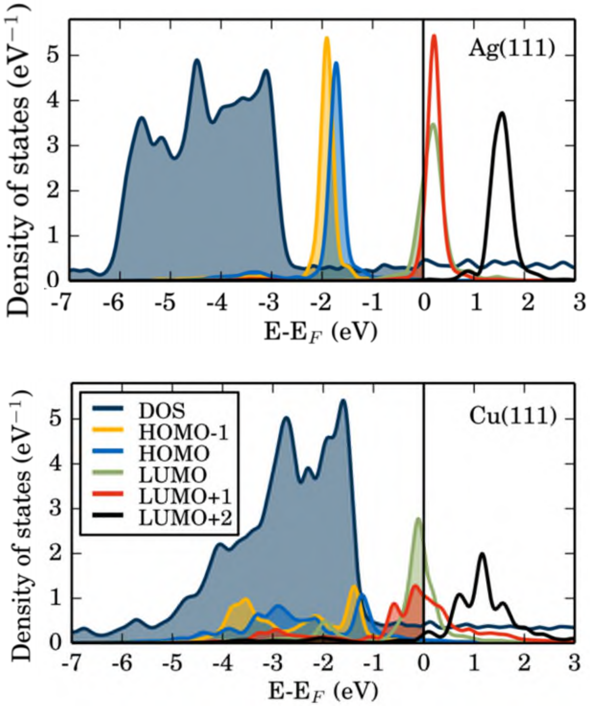
Blasting surfaces with X-rays



Klein et al., J. Phys.: Condens. Matter 33, 154005 (2021)
Diller et al., J. Chem. Phys. 146, 214701 (2017)

Surface Chemical Bonding – Quo Vadis?





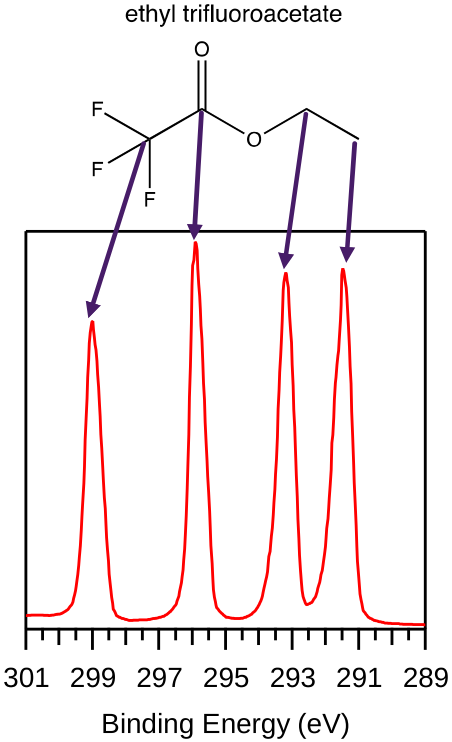
Hybridisation and charge transfer

Müller, Diller, Maurer, Reuter, J. Chem. Phys. 144, 024701 (2016)

Diller et al., J. Chem. Phys. 146, 214701 (2017)

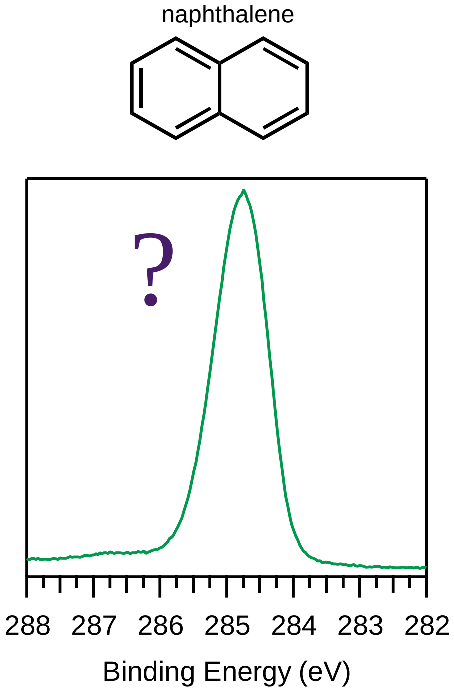
Problem 1: Relative Peak assignment

- Multiple chemical environments
- Clearly resolved peaks



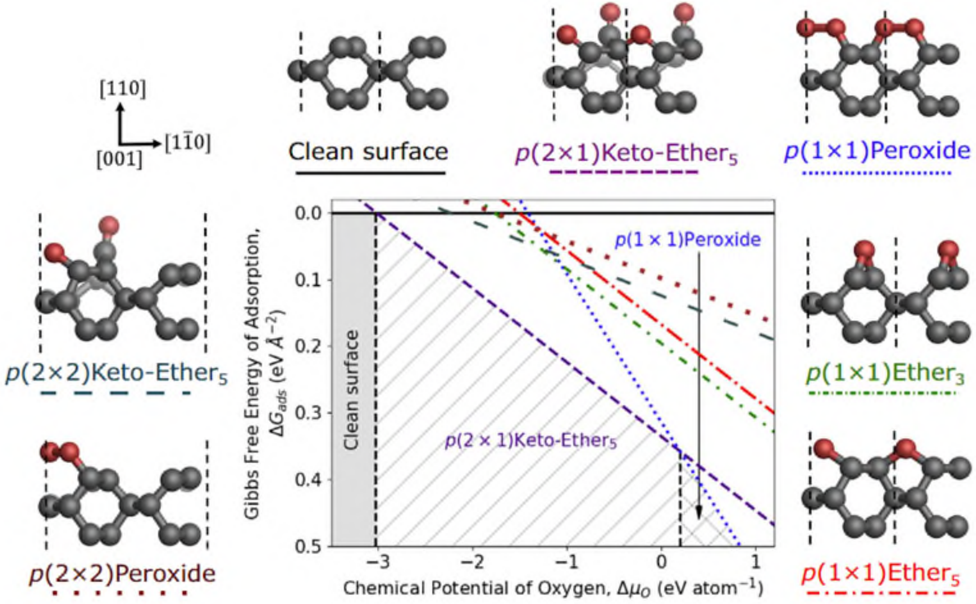
C1s XPS

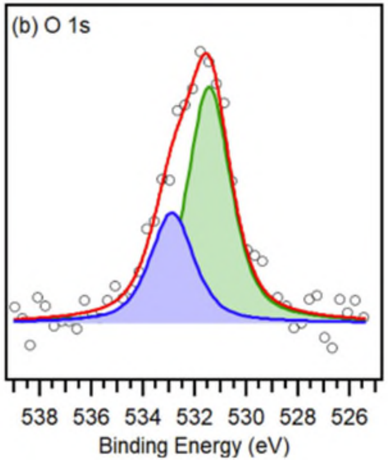
- π-conjugated molecule
- All carbons have similar chemical environment
- Unable to distinguish due to experimental resolution



Problem 2: Absolute referencing of binding energies

Example: Oxygen surface termination of diamond (110)





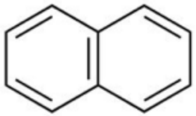
Absolute binding energy calculations

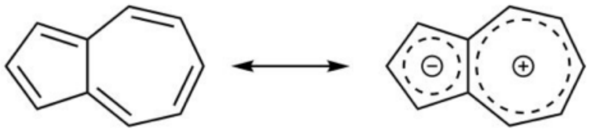
See talk by
Dylan Morgan

FHI-aims
The ab initio materials simulation package

Chaudhuri, Hall, et al., Communications Materials **3**, 6 (2022)

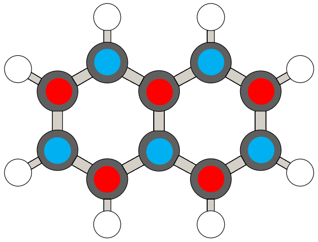
Topology and Spectroscopy



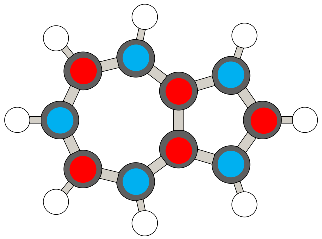


Naphthalene (Np)

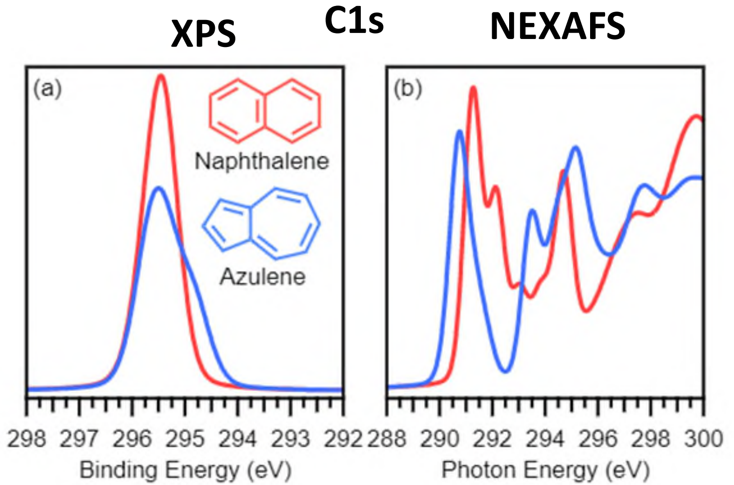
Azulene (Az)



alternant

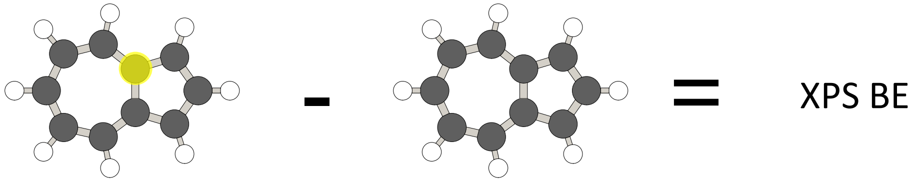


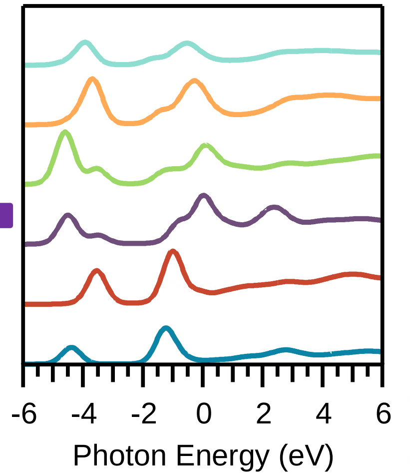
non-alternant

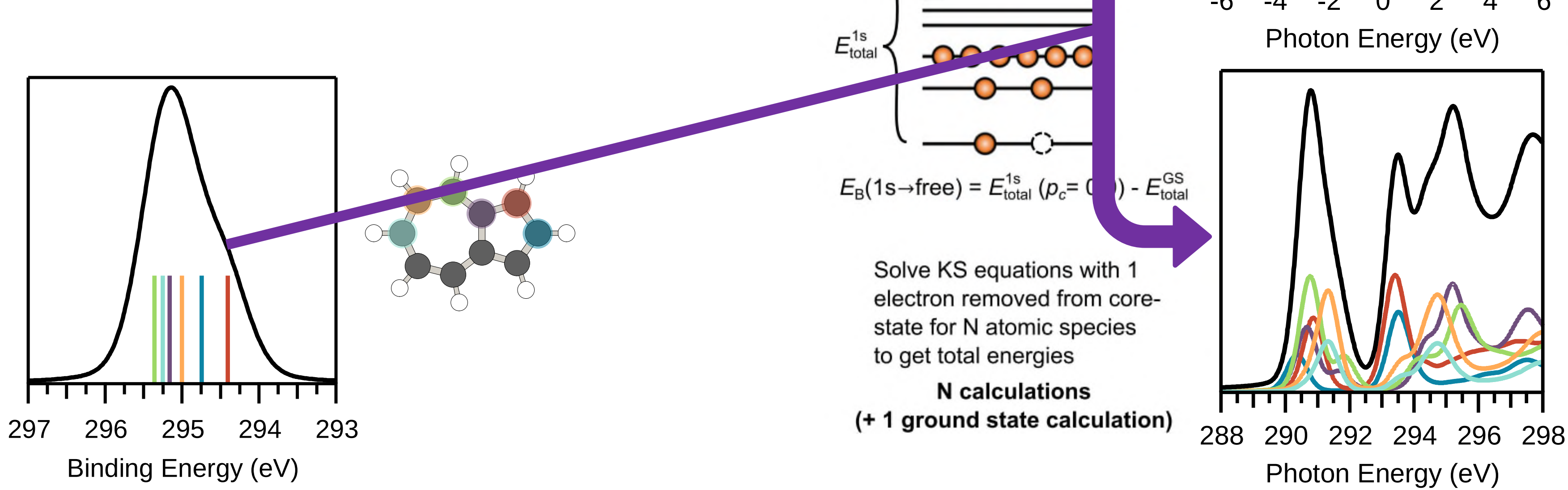


Klein et al., Phys. Rev. X 9, 011030 (2019)

Core-level Simulation of XPS & NEXAFS



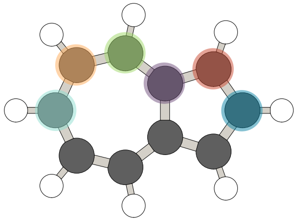




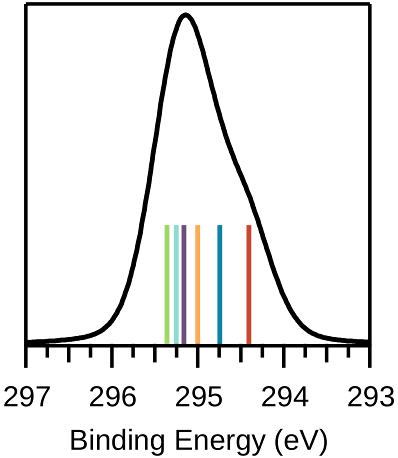
T. Mizoguchi, I. Tanaka, S. Gao and C. J. Pickard, *J. Phys. Condens. Matter* **21**, 104204 (2009)
B. P. Klein, S. J. Hall and R. J. Maurer, *J. Phys. Condens. Matter* **33**, 154005 (2021)

CASTEP

Unpicking spectral contributions

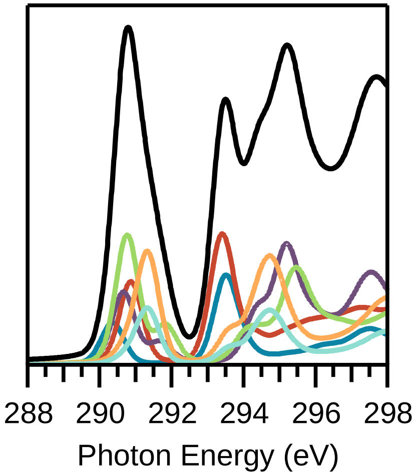


XPS

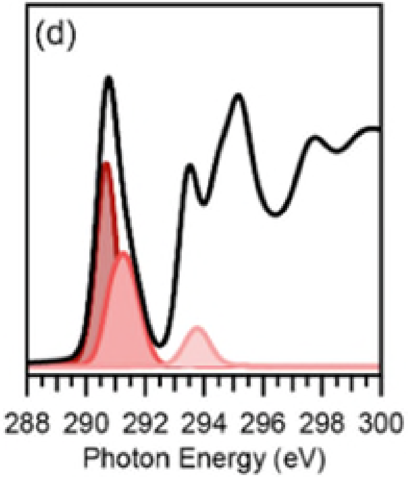


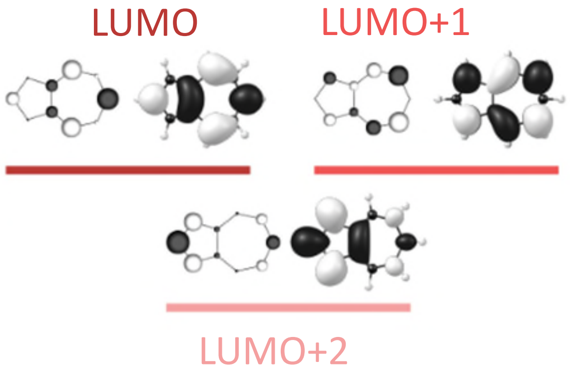
NEXAFS

Initial states



Final states





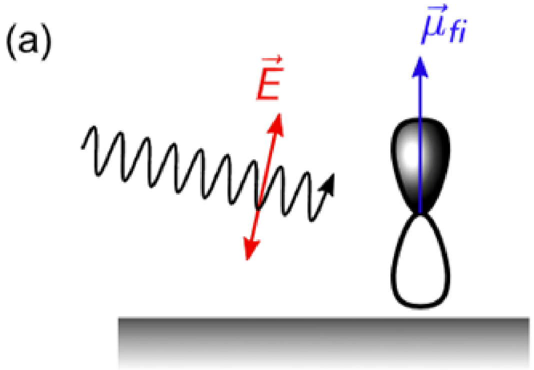
Hall et al., J. Phys. Chem. C 127, 1870–1880 (2023)

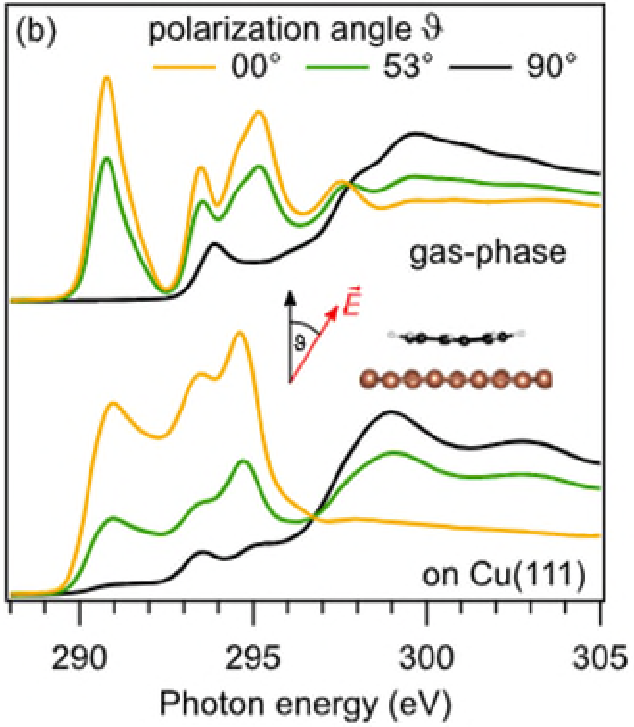
Klein et al., J. Phys. Condens. Matter 33, 154005 (2021)

Orientational/polarization dependence

$$\sigma_i(h\nu) \propto \sum_f |\langle \psi_f | \mathbf{e} \cdot \mathbf{p} | \psi_i \rangle|^2 \delta(h\nu - \underbrace{(E_f - E_i)}_{\Delta E_{fi}})$$

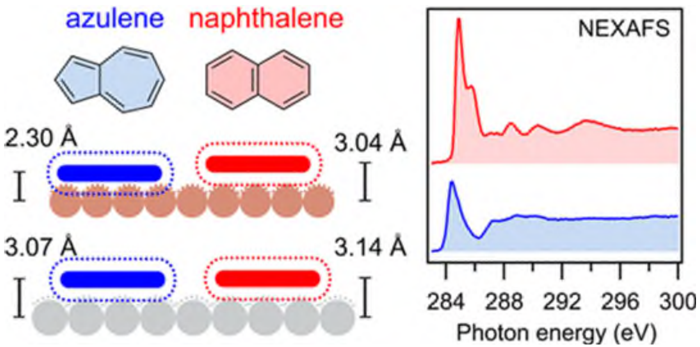
$$\mu_{fi} = |\langle \psi_f | \mathbf{e} \cdot \mathbf{p} | \psi_i \rangle|^2 \approx |\mathbf{e} \cdot \underbrace{\langle \psi_f | \mathbf{p} | \psi_i \rangle}_{\mathbf{D}_{fi}}|^2$$

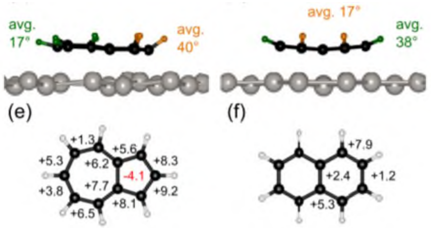


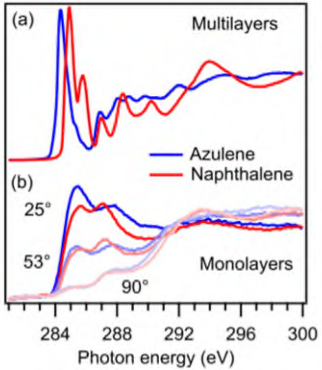


Klein et al., J. Phys. Condens. Matter 33, 154005 (2021)

Naphthalene Azulene



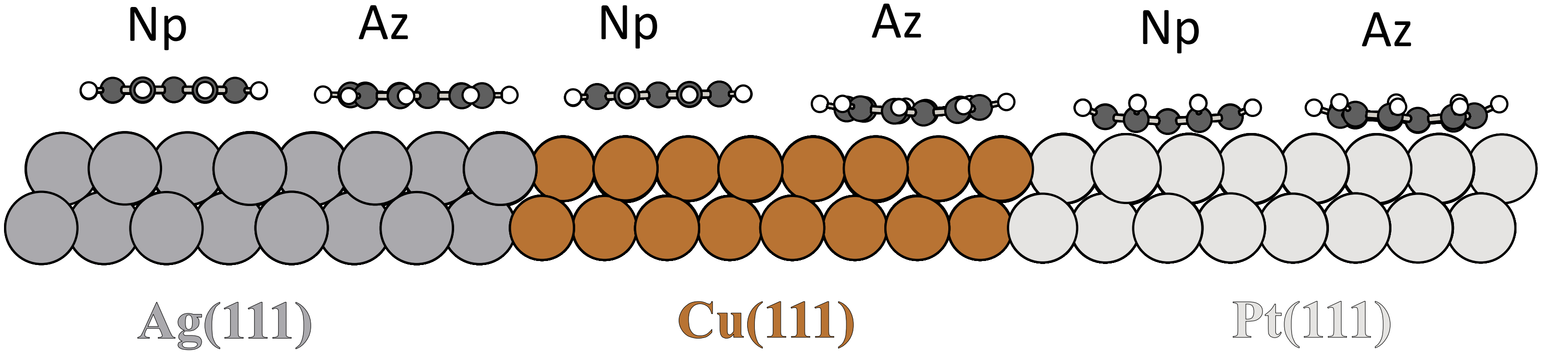




Michael Gottfried (Marburg)

Benedikt Klein

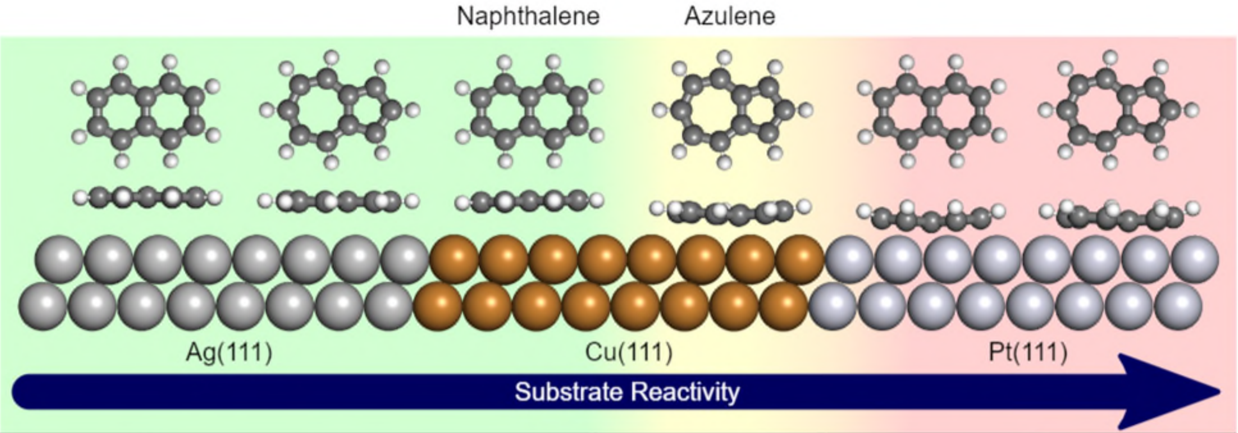
Sam Hall



Detailed experiment/theory characterisation: XPS, NEXAFS, XSW, UPS, TPD, LEED, STM, AFM, DFT, ...

JPCC 123, 29219-29230 (2019) PRX 9, 011030 (2019) Chem. Matter 32, 1041-1053 (2020)

Naphthalene & Azulene: a playground to understand surface chemistry

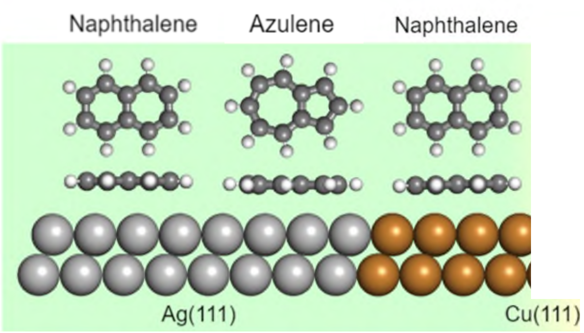


Adsorption Energy (kJ/mol)	118	128	135	173	298	335
Adsorption Height (Å)	3.10	2.94	2.96	2.33	2.09	2.10
Net Charge Transfer (e)	0.06	0.01	0.06	-0.49	0.03	0.02
Structural Deformation	None	None	None	Weak	Strong	Strong
Molecule-Metal Hybridisation	Weak	Weak	Weak	Intermediate	Strong	Strong

Category 1 **Category 2** **Category 3**

Hall et al., J. Phys. Chem. C 127, 1870–1880 (2023)

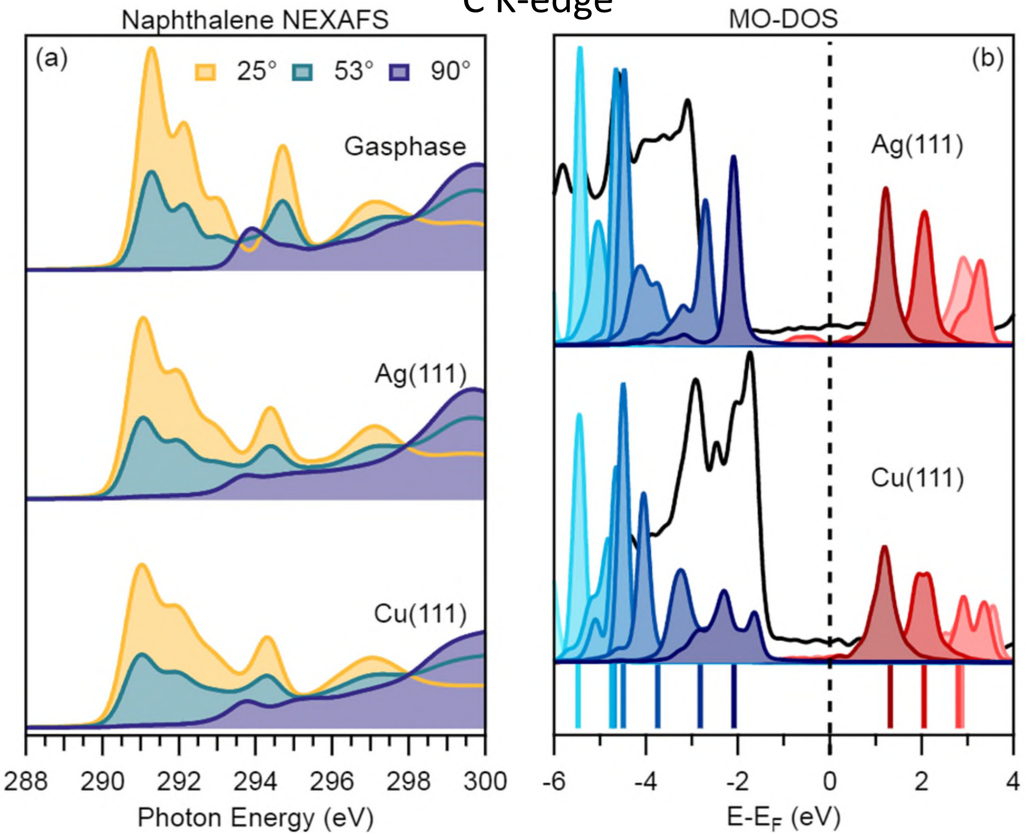
Category 1



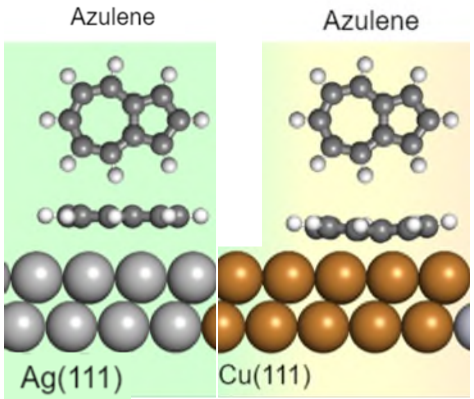
- No significant charge transfer
- Little hybridisation
- Spectra only slightly broadened
- Dichroism unaffected

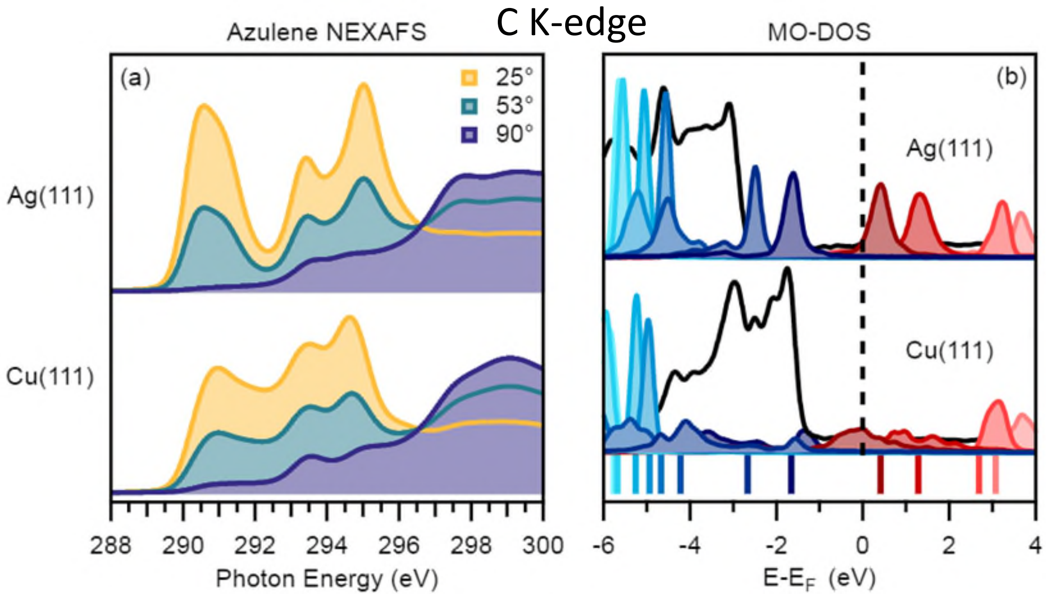
"Physisorption"

C K-edge



Category 2





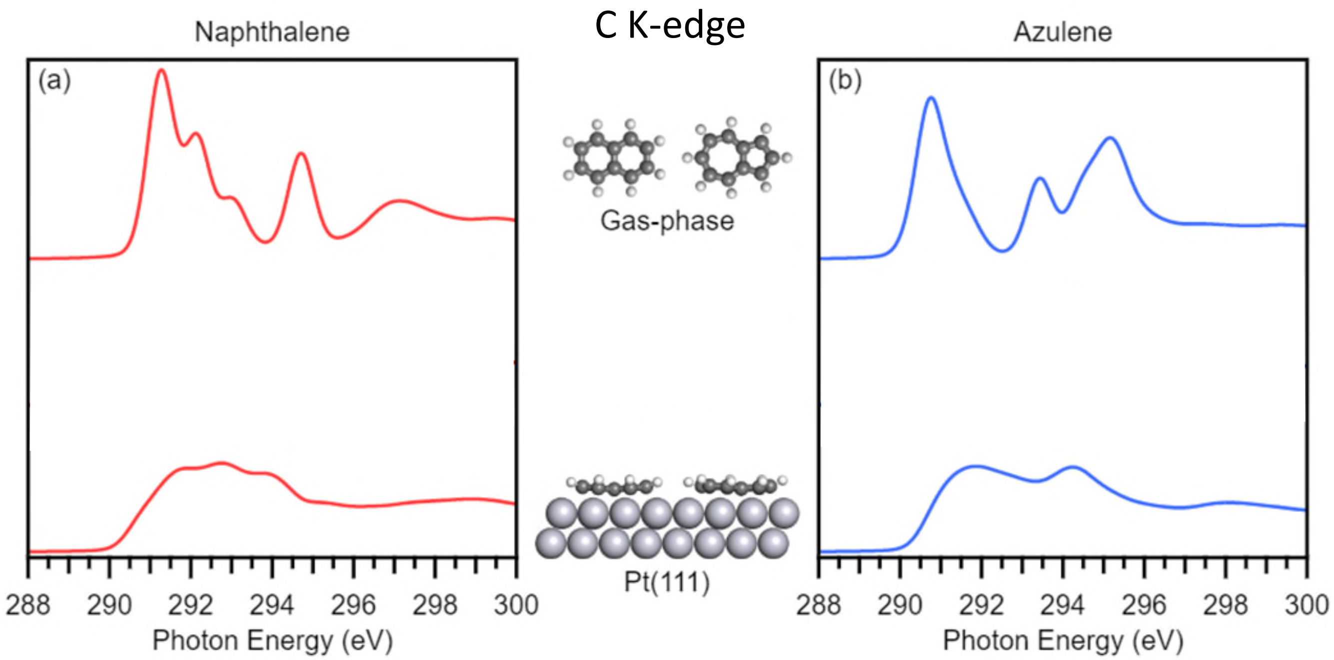
- Hybridisation for both Ag and Cu
- Only Az/Cu shows charge transfer
- Intensity of first peak diminished
- Dichroism also affected
- Neither clear case of "physisorption" nor "chemisorption"

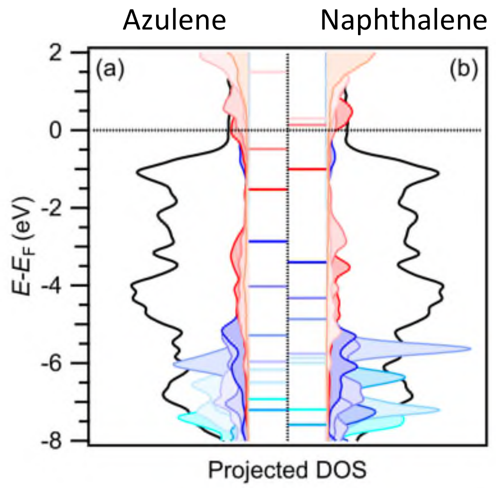
Table 1: Relative intensities of the first 3 peaks seen in the NEXAFS spectra of azulene on Ag(111) and Cu(111) with respect to the corresponding peaks of azulene gas-phase spectrum.

Peak	Relative Intensity	
	Az/Ag	Az/Cu
1	0.65	0.44
2	0.93	1.04
3	0.96	0.82

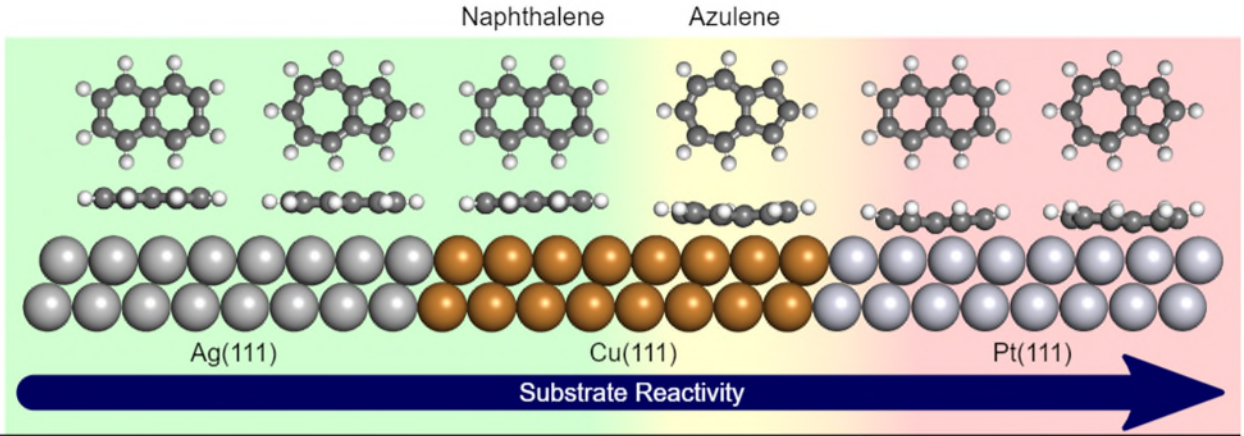
Charge Transfer

Category 3: “Chemisorption”





A playground to understand surface chemistry



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Molecule-Metal Hybridisation	Weak	Weak	Weak	Intermediate	Strong	Strong

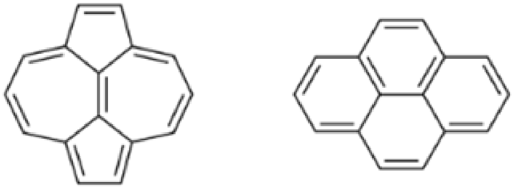
Category 1 **"Physisorption"**

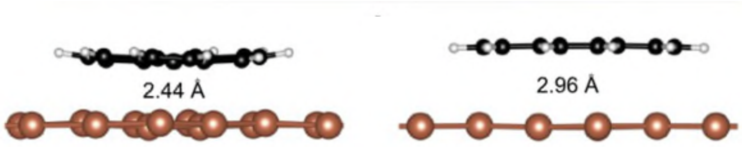
Category 2 **Charge Transfer**

Category 3 **"Chemisorption"**

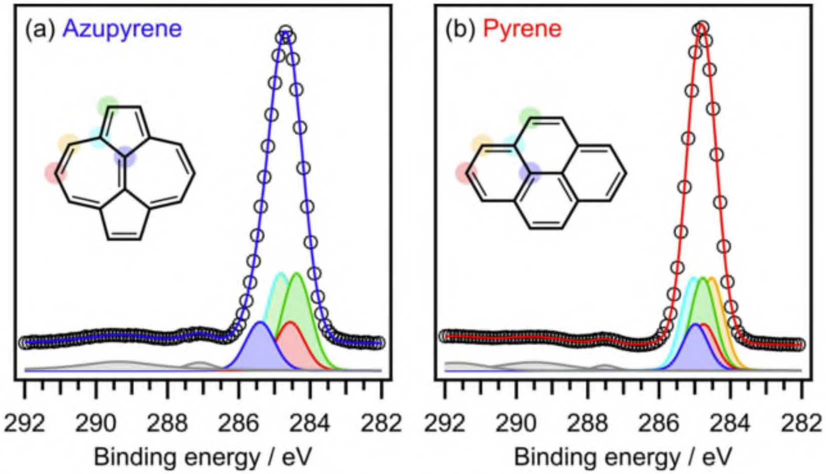
Azupyrene and Pyrene

@Cu(111)

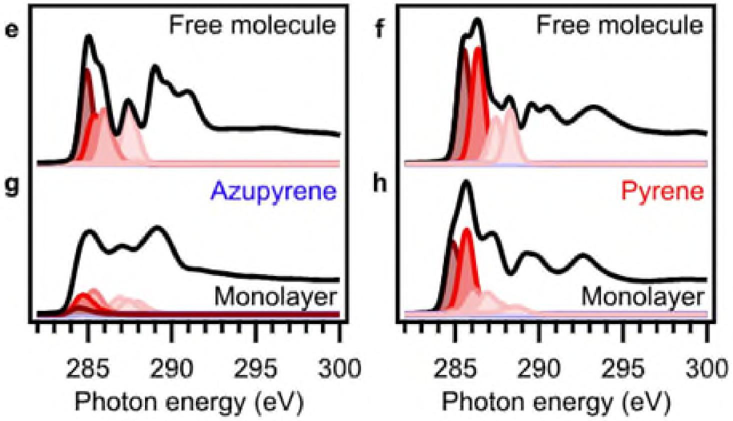




XPS



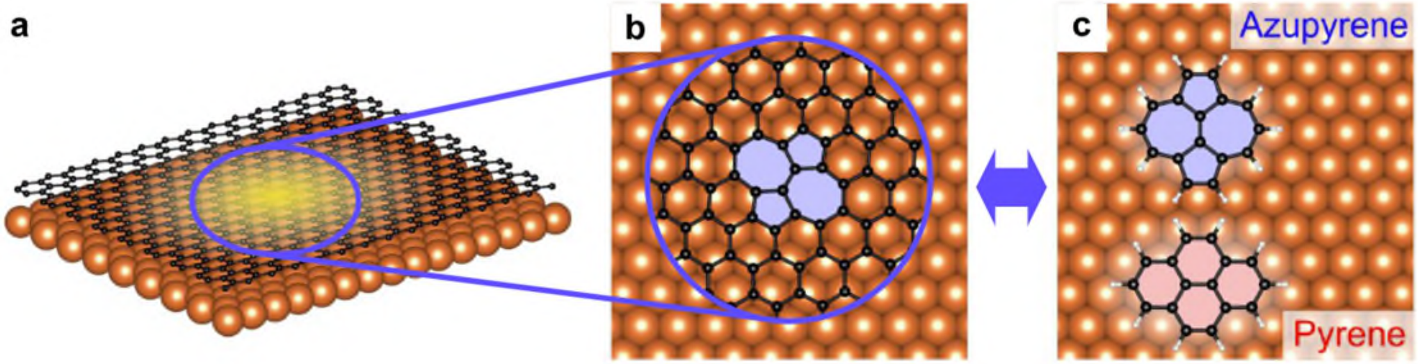
NEXAFS

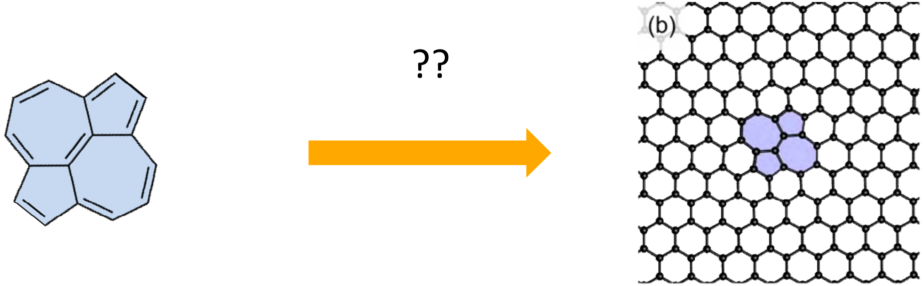


Klein et al., ChemPhysChem 22, 1065-1073 (2021)

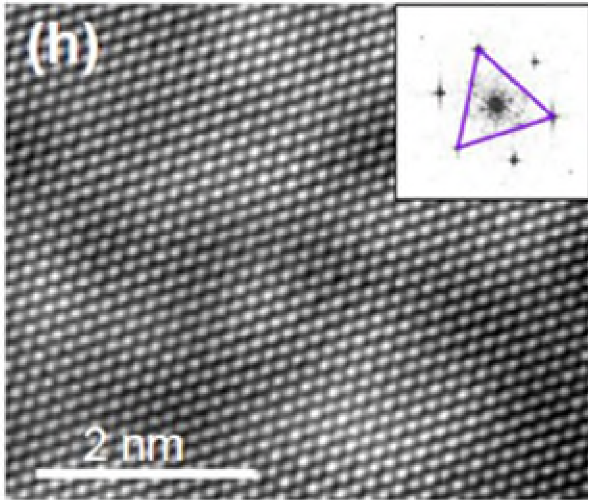
Klein et al., ACS Nano, 16, 8, 11979–11987 (2022)

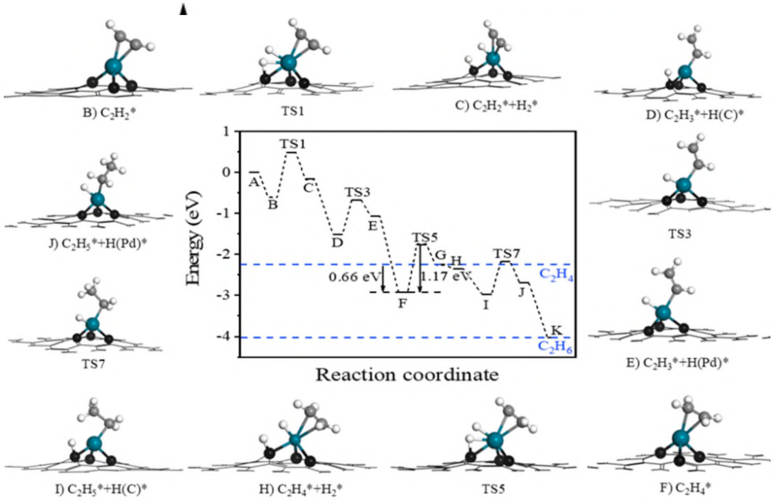
Azupyrene – a molecular model of a Stone-Wales defect



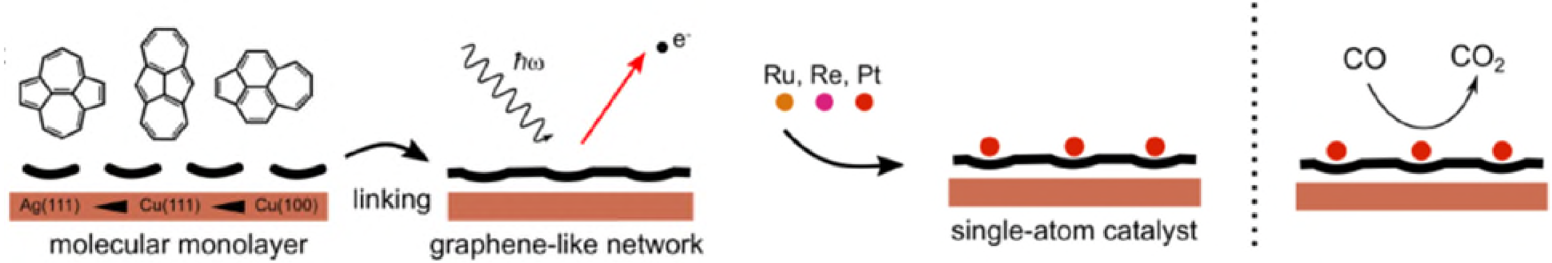


The Beauty of Imperfection: Topological Design of Defective Graphene

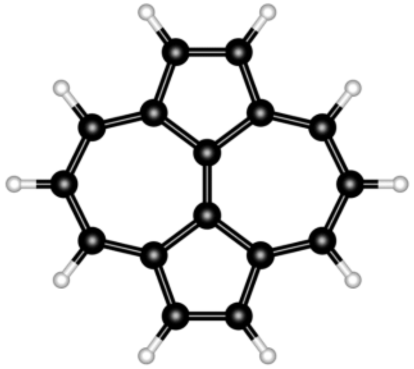




F. Huang, et al., J. Am. Chem. Soc., 2018, 140, 13142-13146

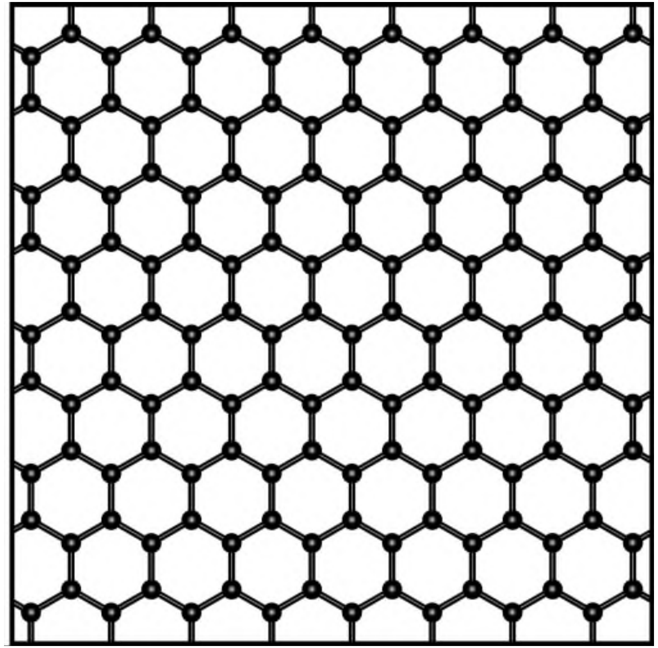


Growing defective graphene from azupyrene?



Azupyrene

High T deposition on Cu(111)



Benedikt Klein

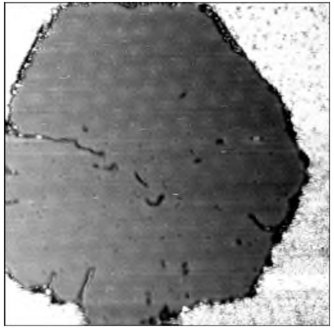
Matt Stoodley

David Duncan

Appl. Phys. Lett. **121**, 191603 (2022); doi: 10.1063/5.0122914

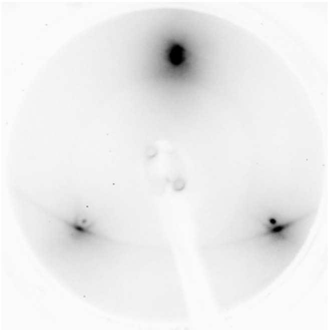
Proving graphene synthesis using azupyrene

1. Moire pattern visible in STM



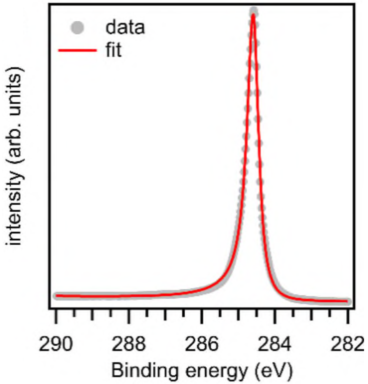
90×90 nm^2

2. Rings in LEED

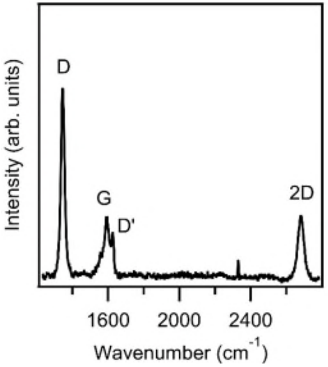


63 eV

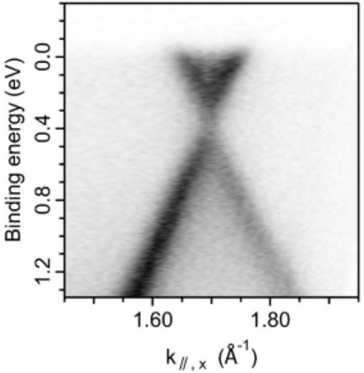
3. Sharp peak in C 1s XPS



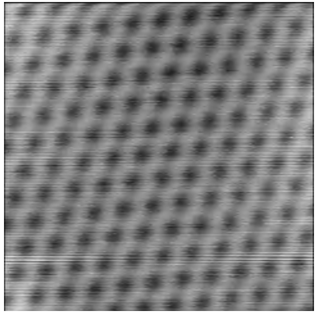
4. Specific Raman peaks



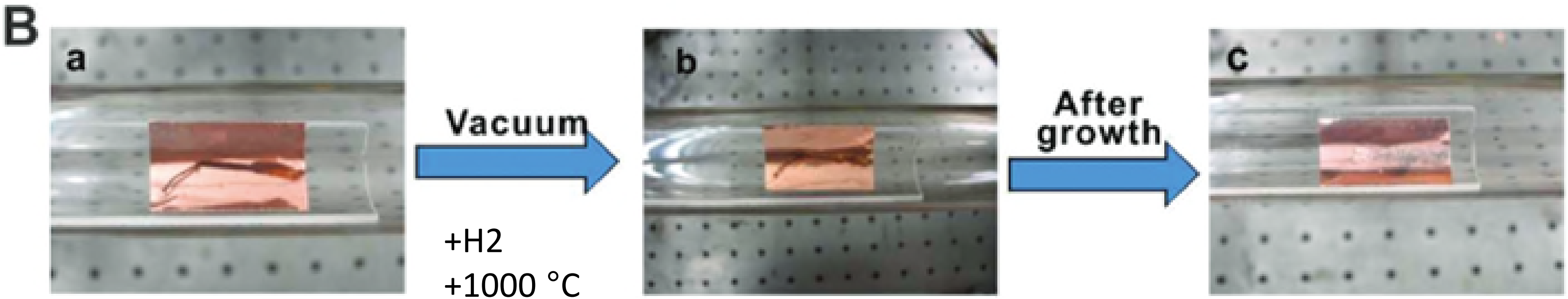
5. Dirac cone in ARPES

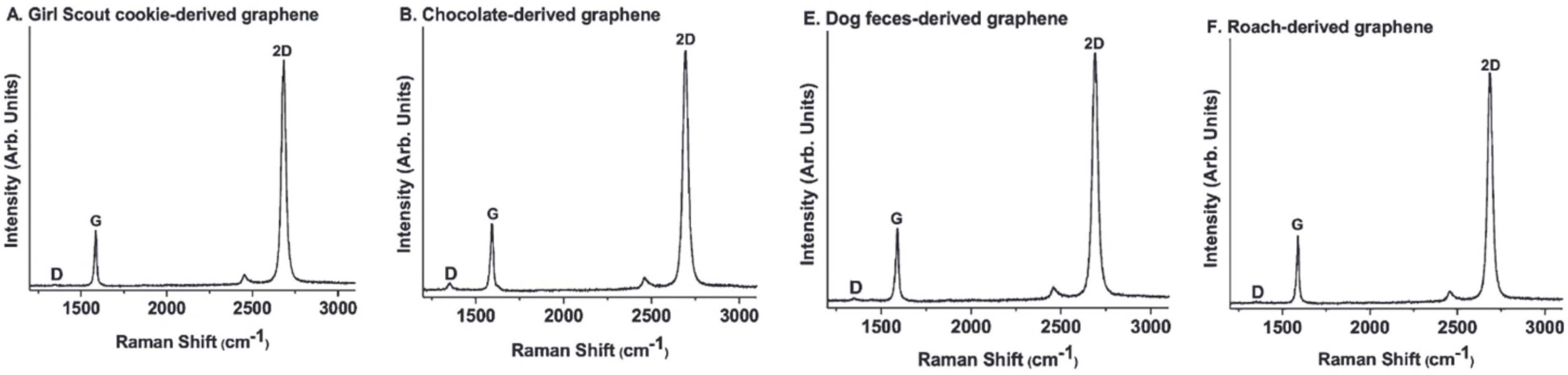


6. Atomic resolution, LT-STM



Is there anything that doesn't convert to graphene on copper?

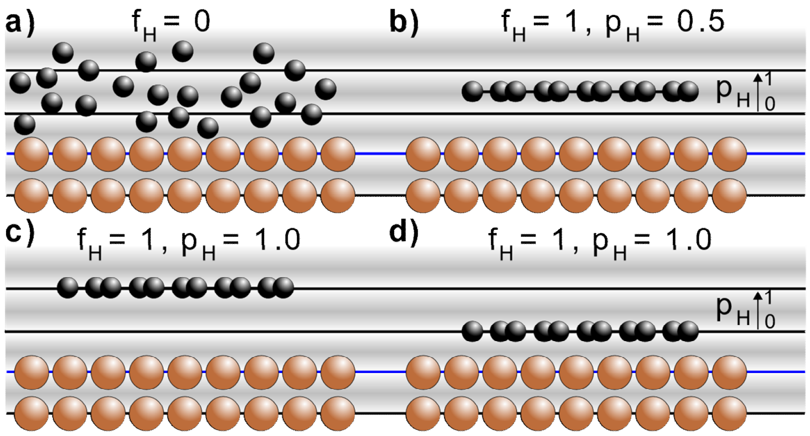


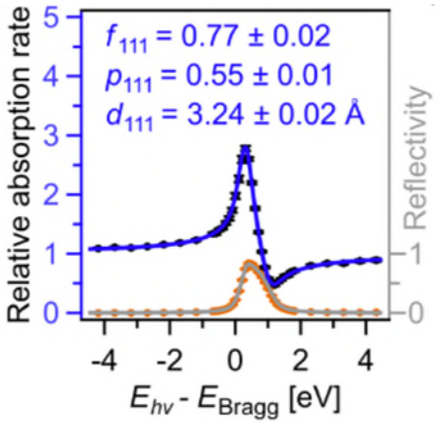


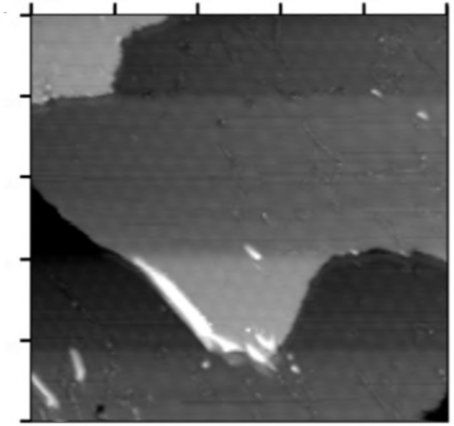
Ruan, Sun, Peng, Tour, ACS Nano 2011, 5, 9, 7601–7607

Normal Incidence X-ray standing waves

CVD grown graphene on Cu(111)





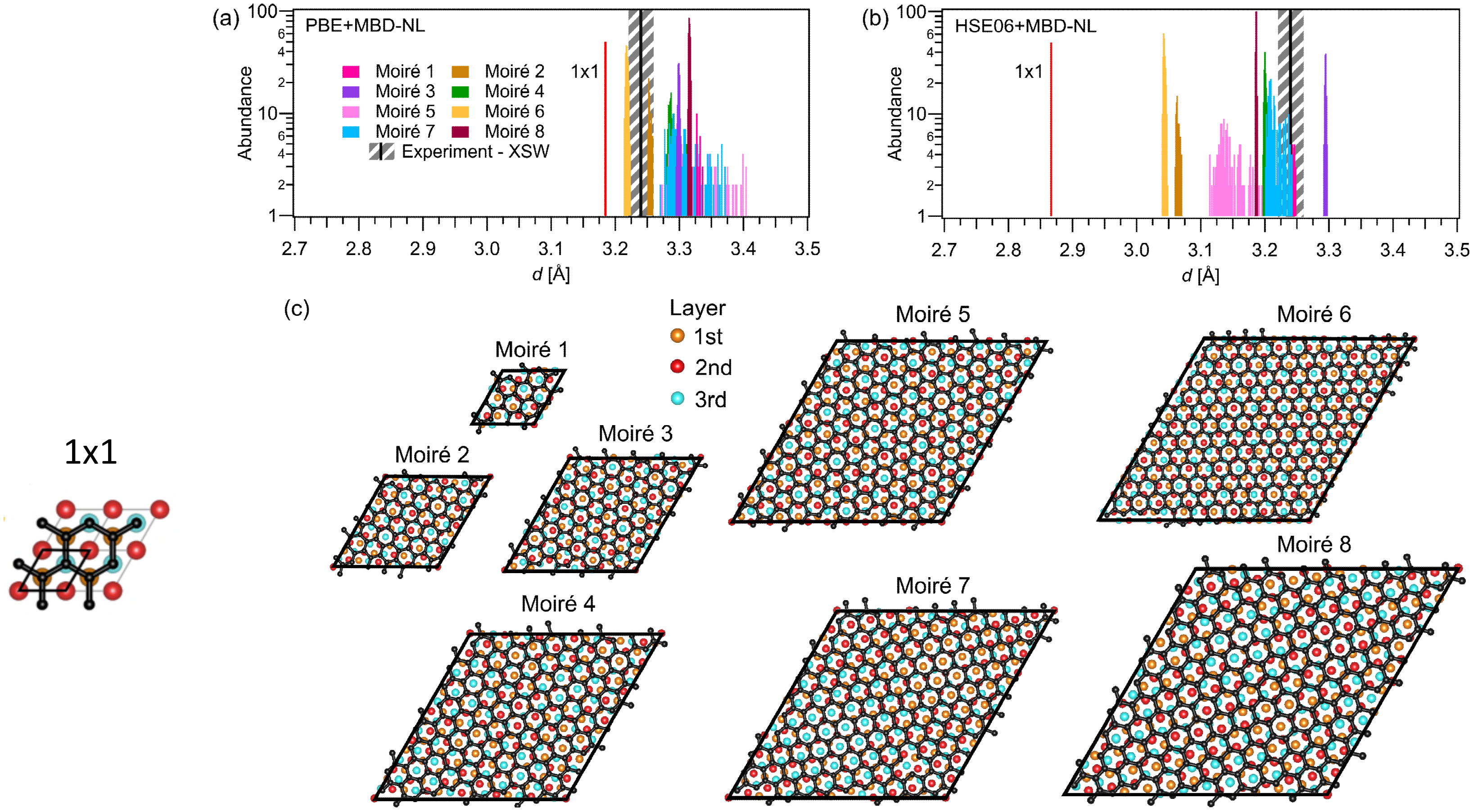


f_H = Coherent fraction

p_H = Coherent position

D. P. Woodruff, Modern Techniques of Surface Science, Cambridge University Press, Cambridge.

Stoodley et al., Phys. Rev. Lett. 132, 196201 (2024)

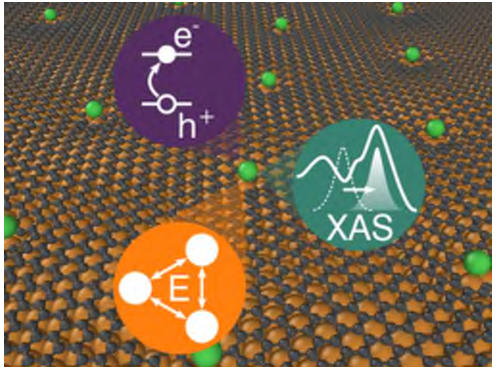


Stoodley et al., Phys. Rev. Lett. 132, 196201 (2024)

Deliberate imperfection

Topological Defect Design in 2D materials

LEVERHULME TRUST



Thank you for your attention!

Theory

Reinhard Maurer (Warwick)

Spectroscopy

David Duncan (Diamond/ Nottingham)

Imaging

Alex Saywell (Nottingham)

Synthesis

Christian Nielsen (QMUL)