Fullerenes on Silicon: Imaging, Spectroscopy, and Manipulation

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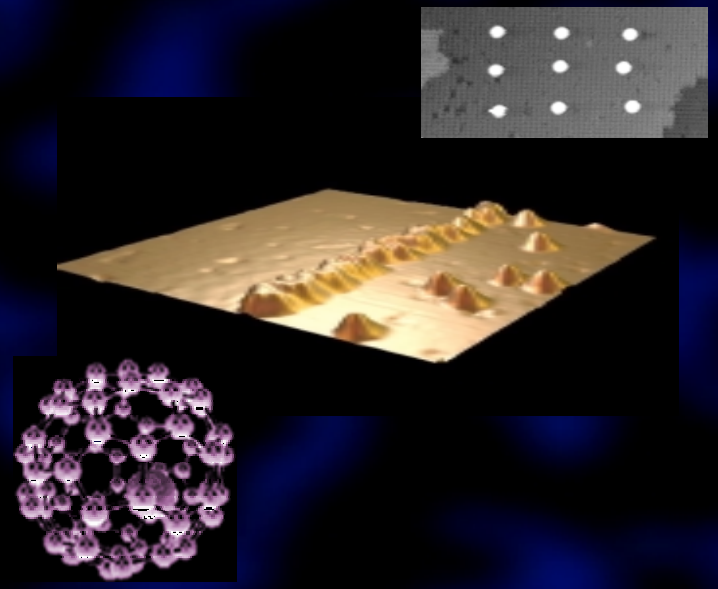

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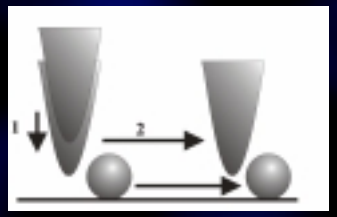
OVERVIEW

- Research in the Nottingham Nanoscience group.
- Molecular manipulation: pushing and pulling.
- Correlating structural and electronic properties: synchrotron radiation spectroscopy
- $Ce@C_{82}$: determining the cage-atom coupling

Collaborations, acknowledgements and a big ‘thank you’…….



Molecular manipulation and fullerenes

Current Nanoscience group members
Karina Schulte
Mick Phillips (PhD 2000 -)
Rich Woolley (PhD 2001 -)
James O’Shea

Past Nanoscience group members
Michael Hunt (Durham from 01/01/03)
Dave Keeling (PhD 1999 - 2002)
Mike Taylor (PhD 1998 - 2002)
Martin Humphry (PhD 1997 -2000)
Andrew Dunn (PhD 1996 – 1998)
Ron Ma (PhD 1997 -1999)
Martin Upward (PhD 1997 -2000)
Matt Butcher (PhD 1997 – 2000)
Brad Cotier (PhD 1997 – 2000)
Fran Jones (Post-doc 1998)

Collaborators
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Peter Gill (Chemistry, Nottingham)
P. Birkett (Manchester)
Mike Chesters (Chemistry, Nottingham)
L. Dunsch (Dresden)
J. Greer (NMRC)
J. Twamley (Maynooth)
VR Dhanak, G.Miller, JA Purton, S. Patel,
A Wander (Daresbury Lab.)
Sussex Fullerene group

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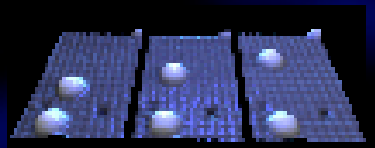
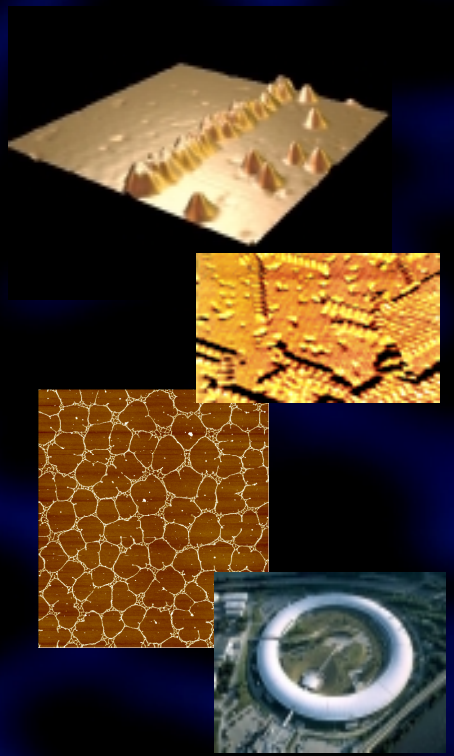
EPSRC
EU Fifth Framework
Royal Society
Oxford Instruments
NPL

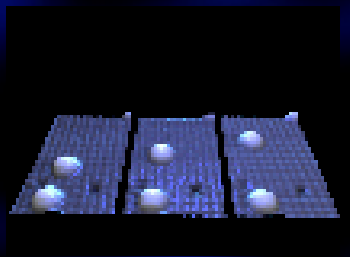
Nottingham Nanoscience Group



Research areas

- Molecular manipulation (PHB, PJM)
- Supramolecular surface chemistry (PHB, JNO)
- Electrospray deposition (JNO)
- Fullerene science (PHB, PJM, JNO)
- Synchrotron spectroscopies (JNO, PJM)
- Near-field optics (PJM, PHB)
- SPM instrument development (PHB, CJM, PJM)
- (Bio)polymers – wetting, crystallization (JSS, PJM)
- Far-from-equilibrium pattern formation (PJM, JSS)
- Colloidal nanoparticles (PJM)
- Biosystems (CJM, JSS, JNO)



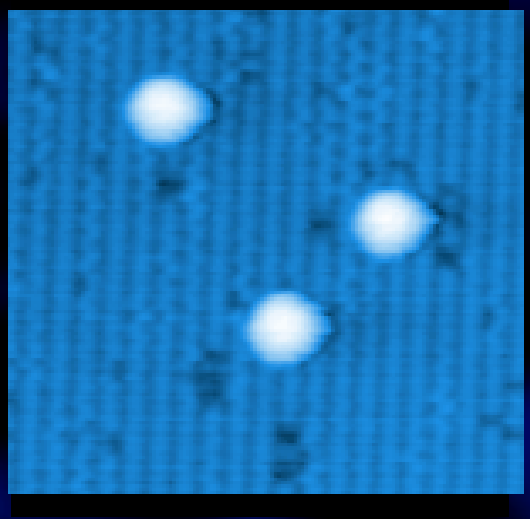


Room temperature molecular manipulation

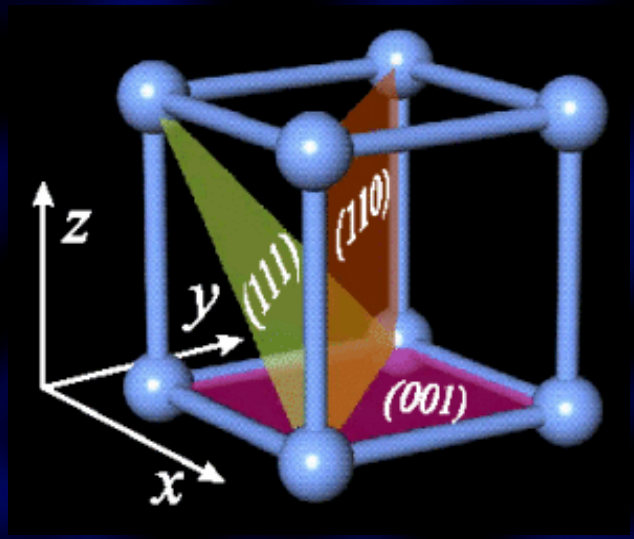
- For room temperature manipulation, there are two important criteria:

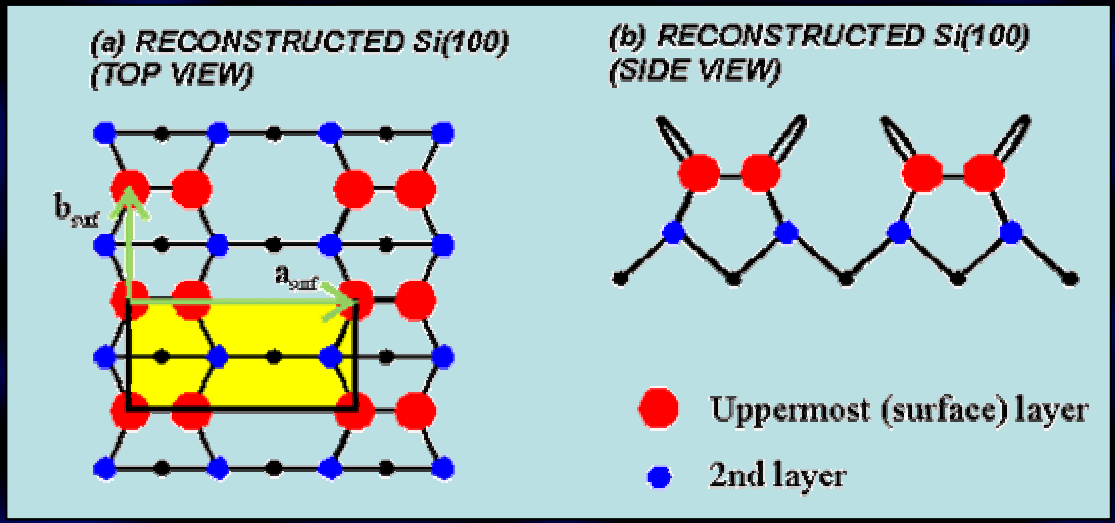
1. High energy barrier so atoms/molecules don't diffuse.
2. Bonding with substrate sufficiently weak so that STM tip can push/pull/slide adsorbates across surface.

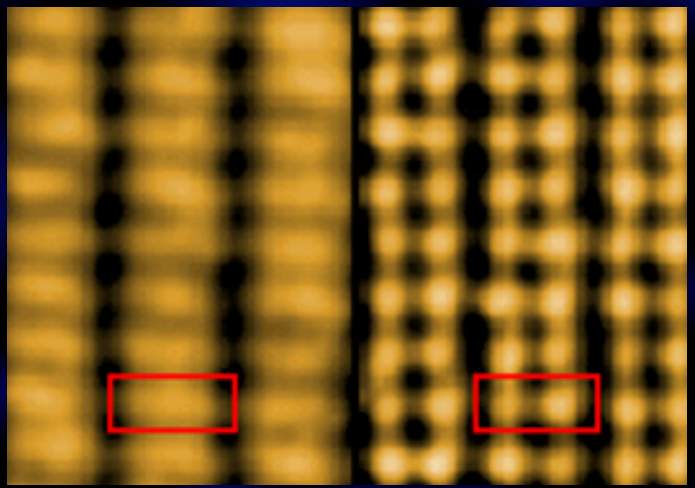
Buckminsterfullerene on Si
is one of the few systems
that satisfies both these criteria



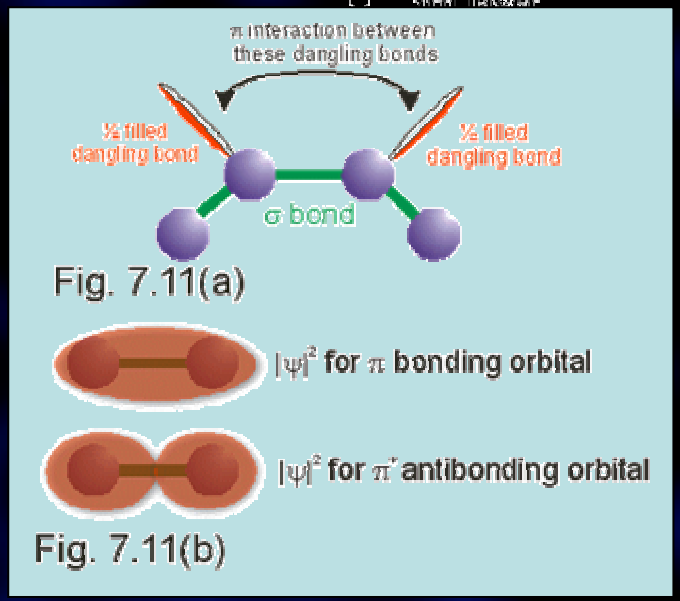
Do we really ‘see’ atoms…..? The Si(100) case

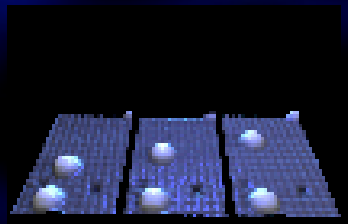






http://hamers/chem.wisc.edu/semi

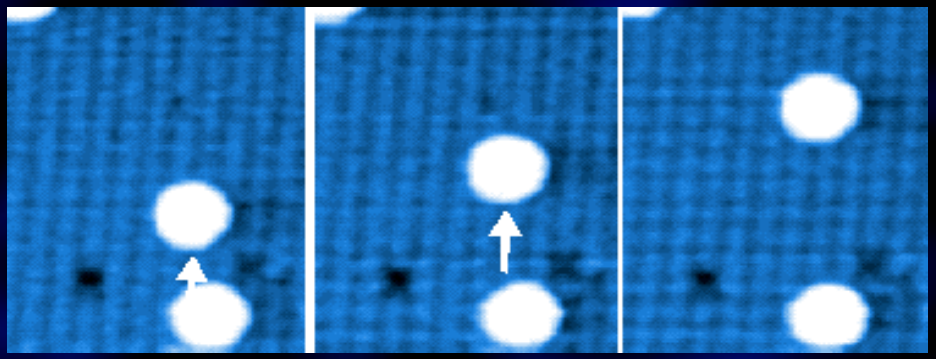




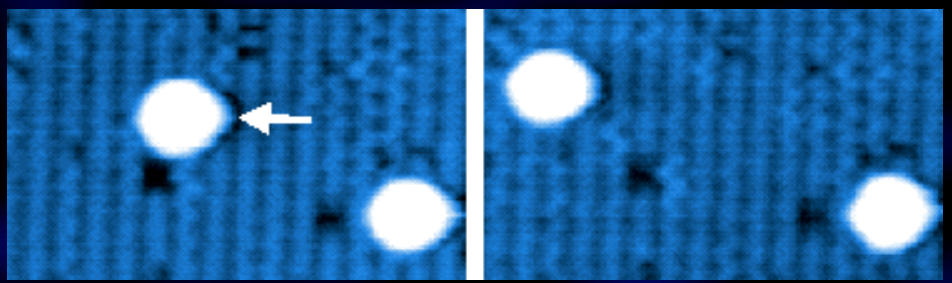
Pushing buckyballs around

*Beton et al., APL **67** 1075 (1995);*
*Moriarty et al., Surf. Sci. **407** 27 (1998)*

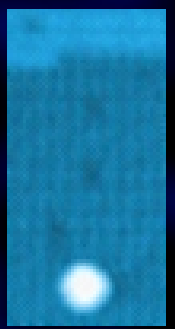
- Parallel to dimer rows……



- Perpendicular to dimer rows……



- …and in both directions

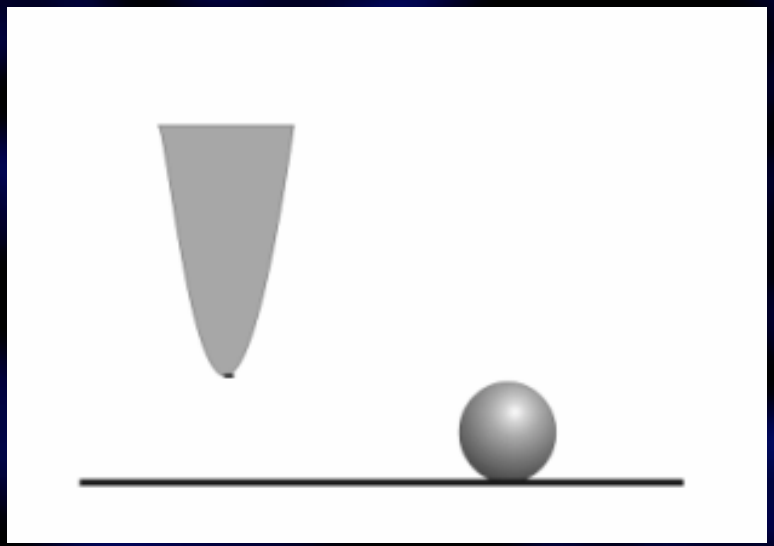


Pushing or pulling C_{60}……?

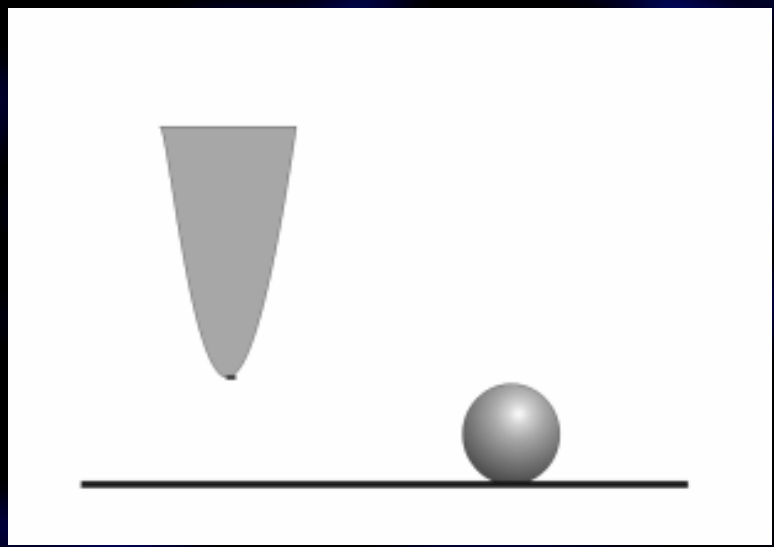
- Must monitor ‘dynamics’ of tip motion *during* manipulation

(Originally suggested by *Bartels et. al.* Phys. Rev. Lett. **79** 4 697 (1997) for LT manipulation)

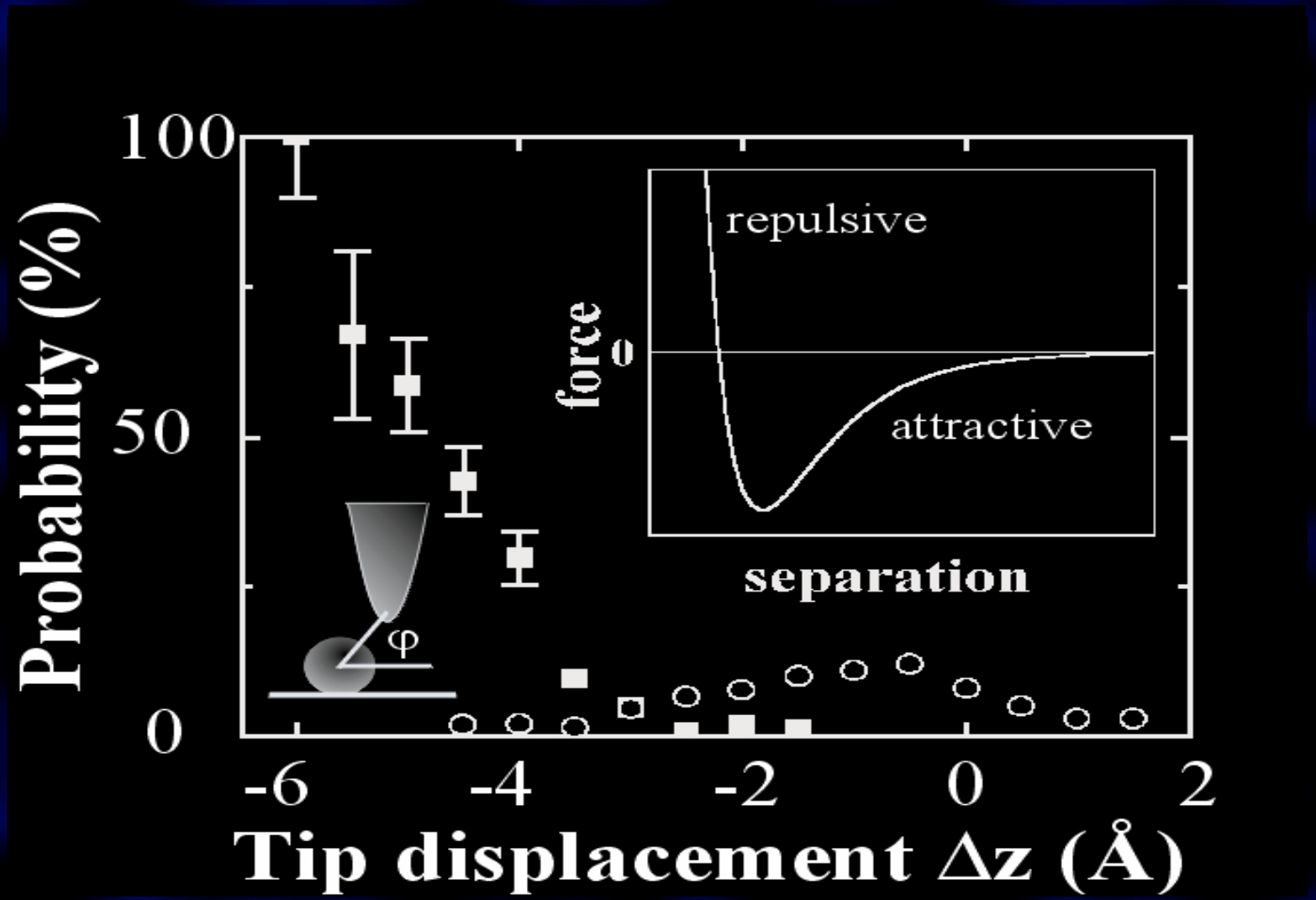
Repulsive mode



Attractive mode



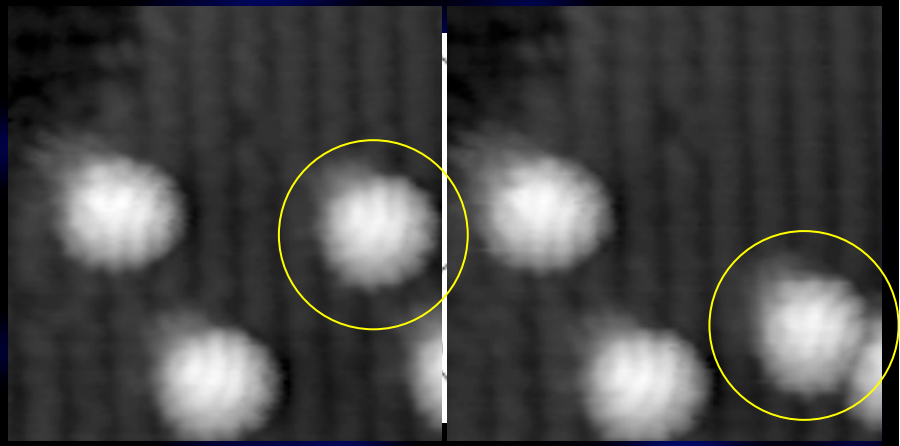
Signatures of attractive and repulsive manipulation



DK Keeling et al., Chem. Phys. Lett. 2003

Rolling or hopping?

- Molecule *rolls* during manipulation process (initial - albeit rather low level - quantum chemistry calculations support idea of molecular rotation)



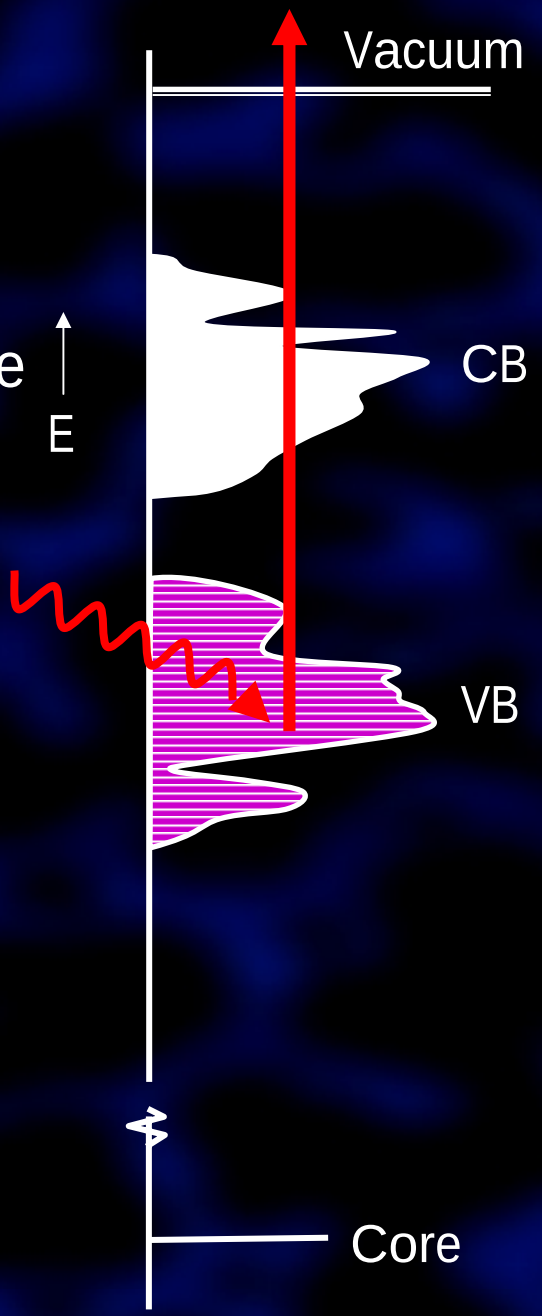
A few words regarding theory….

- In collaboration with Nottingham Computational Chemistry group have explored use of novel empirical density functional (EDF1) + pseudopotential basis set (LANL2DZ) for study of organic-silicon interactions. Computational expense ~ 1 order of magnitude lower than B3LYP
(Phillips et al, Phys Rev B **67** 035309 (2003))

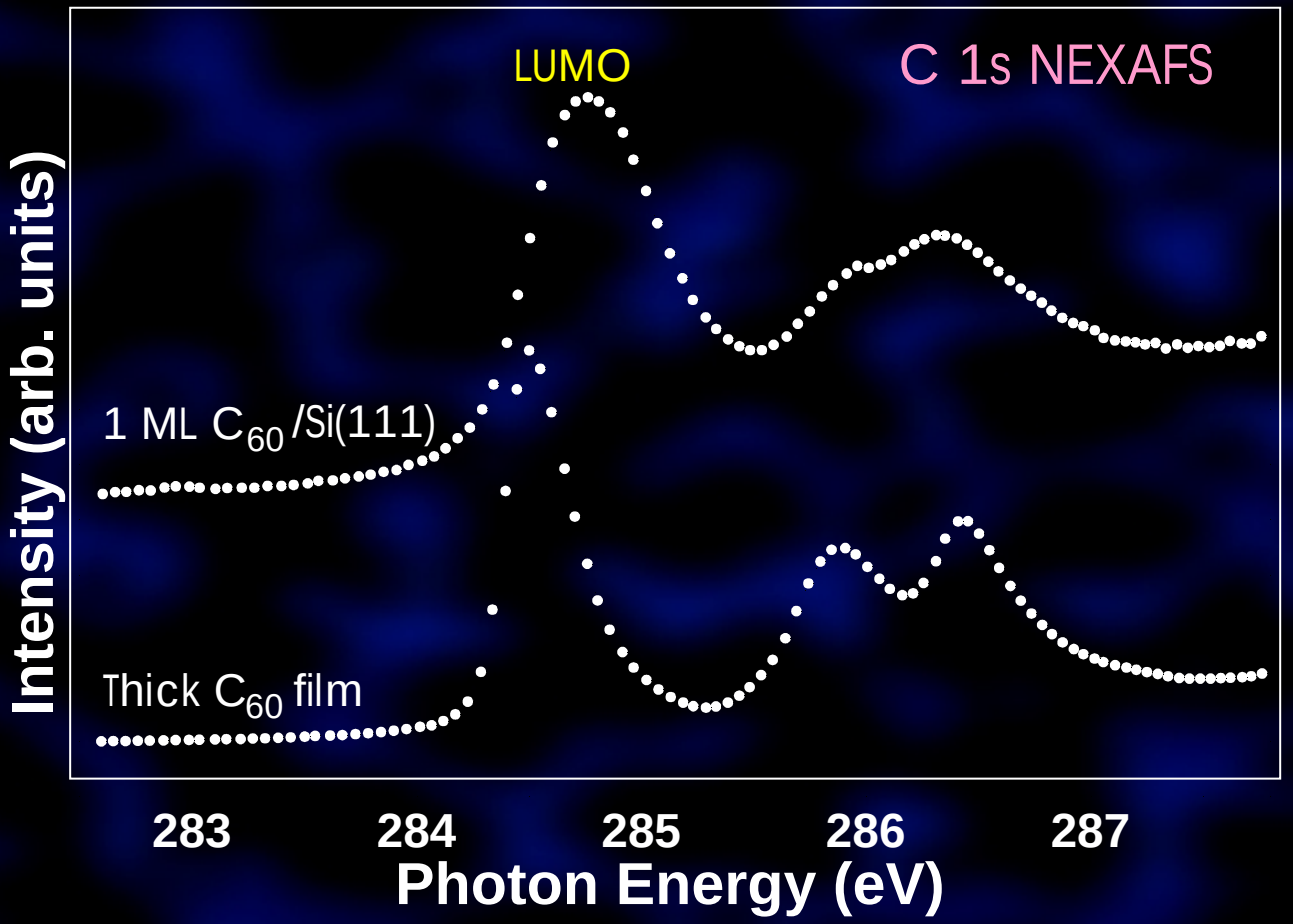
…but C_{60}-Si(100) still very computationally expensive

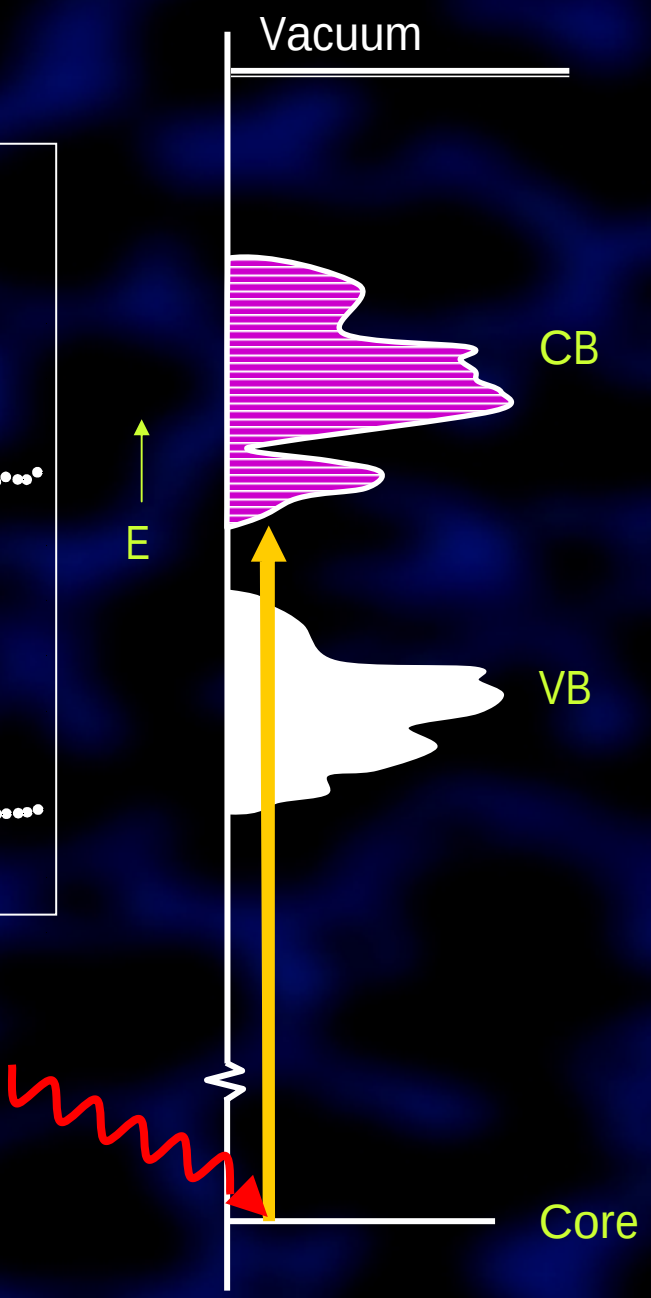
How do fullerenes bond to Si?: SR-based spectroscopies

- Key disadvantages of conventional STM include the inability to carry out detailed (site sensitive) electron spectroscopy *and* the absence of chemical specificity.
- Complement STM data with electron and X-ray spectroscopy.
- Use synchrotron source: tuneable, intense, bright, high (and variable) polarisation.



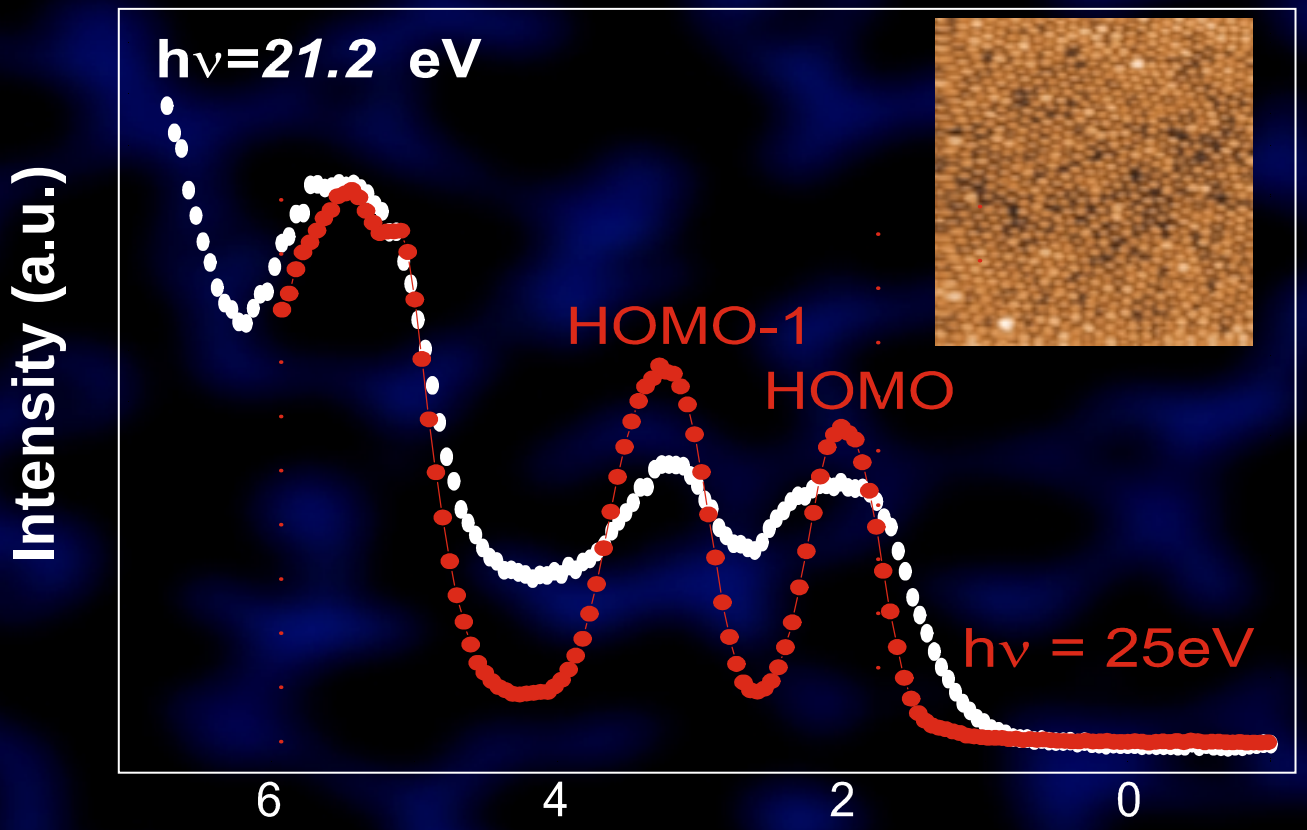
How do fullerenes bond to Si?

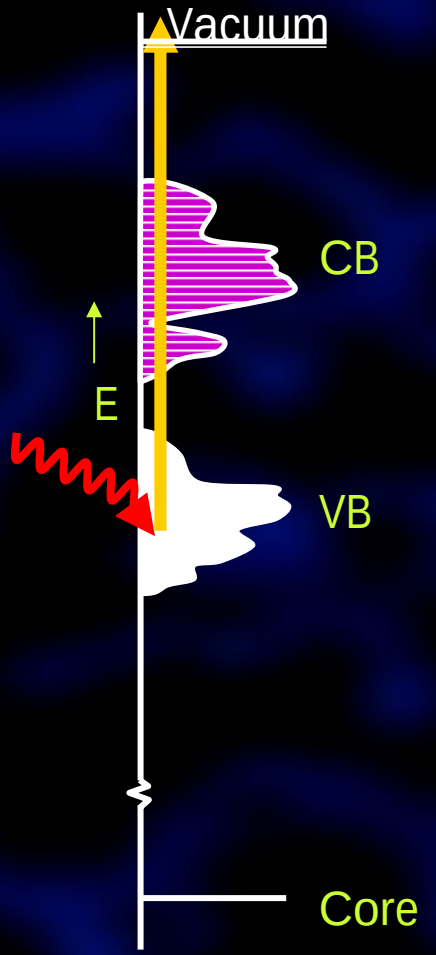




- Use near edge X-ray absorption fine structure (NEXAFS) to probe empty electronic states

How do fullerenes bond to Si?

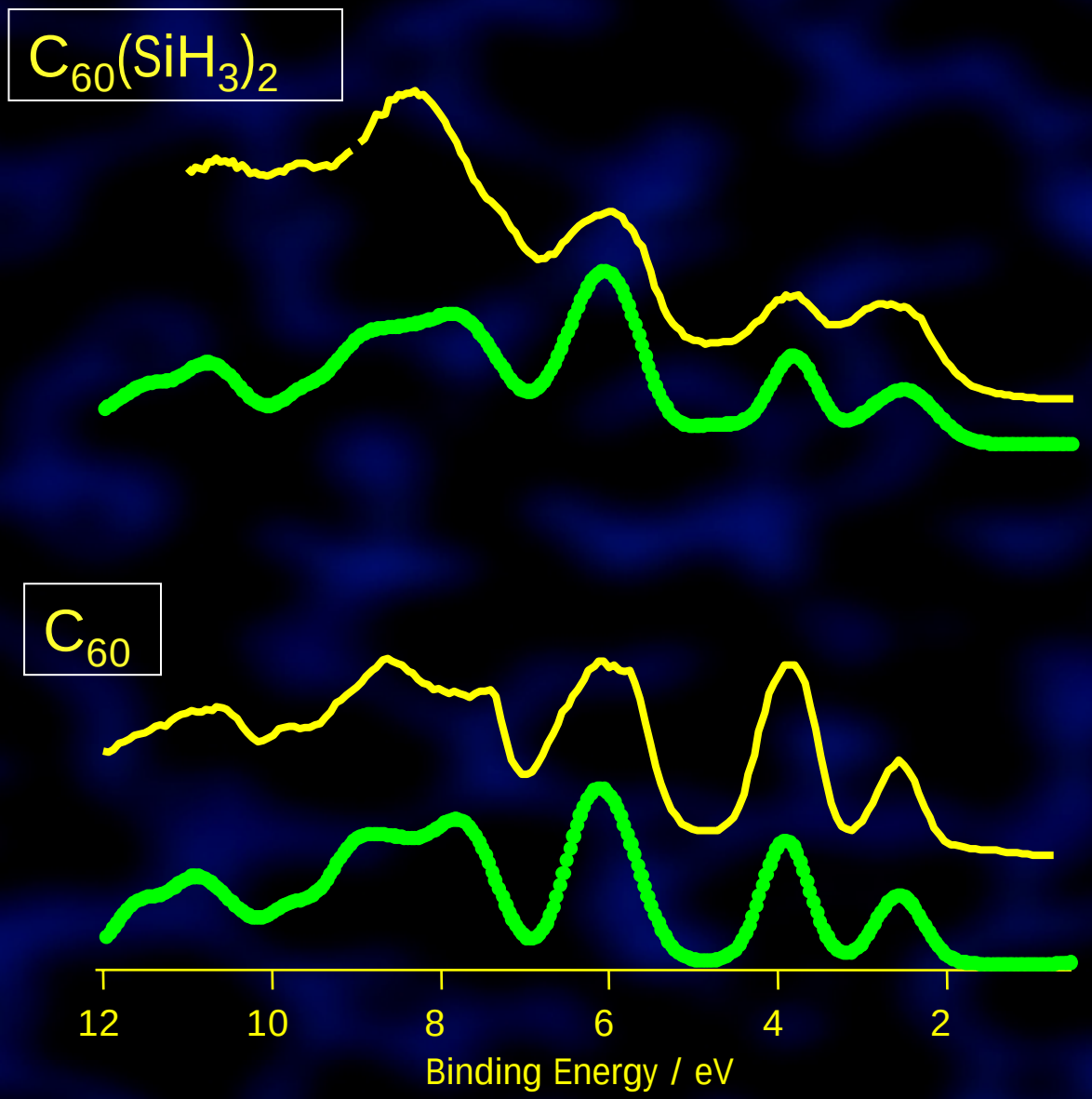




- Fullerenes bond *covalently* to Si (still somewhat controversial result)

*Moriarty et al., Phys. Rev. B **57** 362 (1998);*
de Seta et al., PRB 59 9878 (1999);
Cepek et al., PRB 60 2068 (1999);

Measured and simulated valence bands



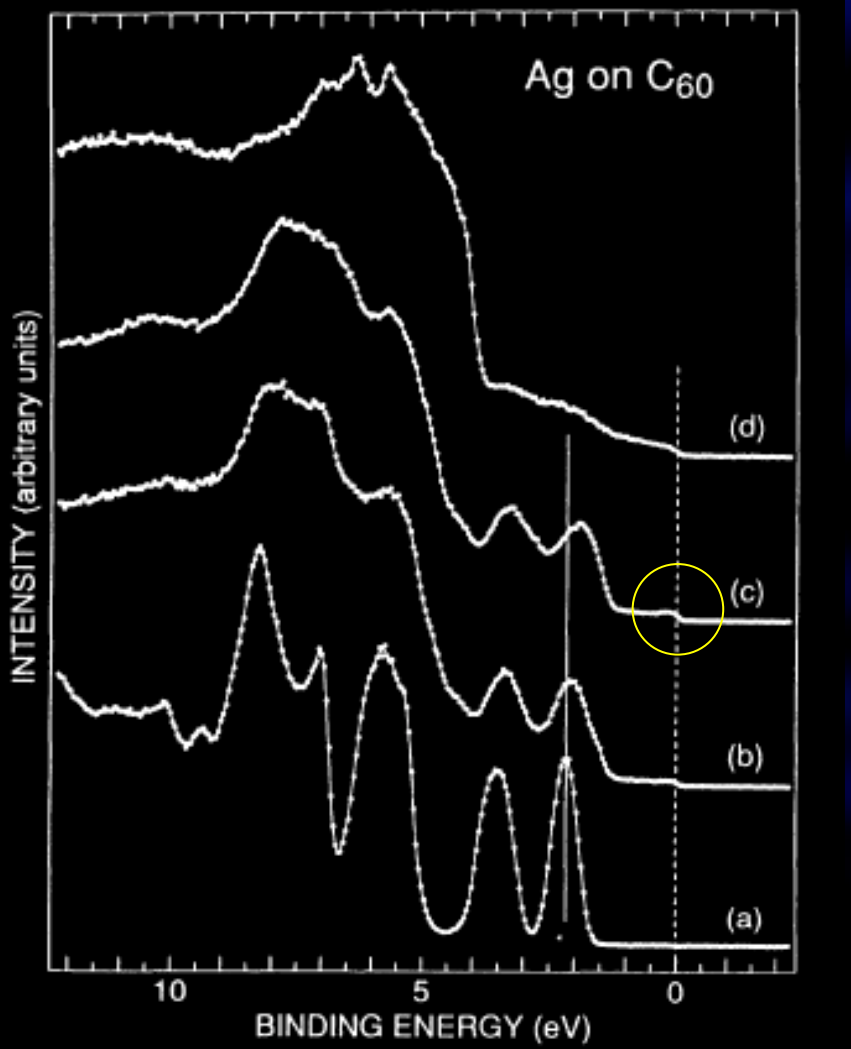
Broadened eigenvalue spectra from B3LYP/ 6-31G*.

Si-C derived feature reproduced well simply by adding two SiH_3 units to the cage: localised covalent bonds.

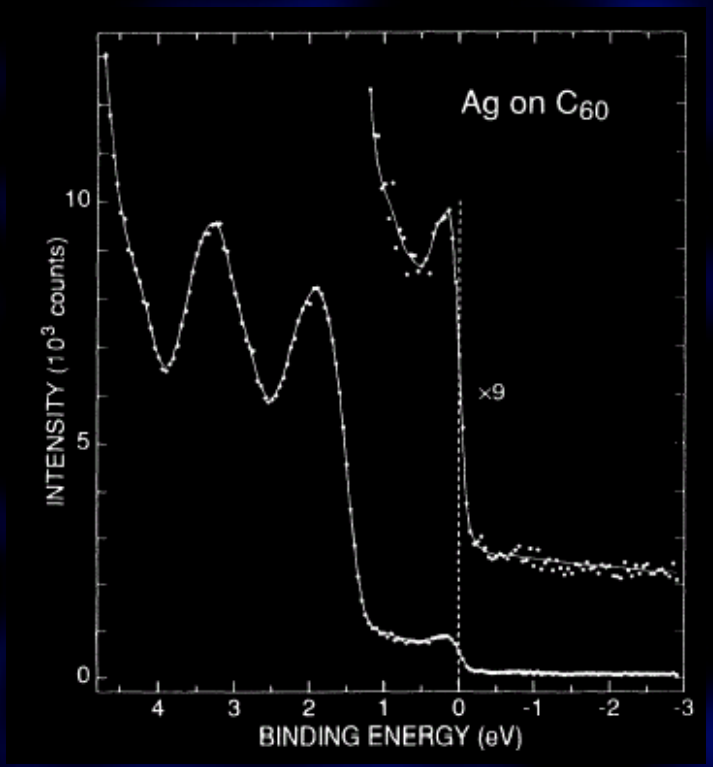
(Phillips et al, unpublished)

Doping fullerite

GK Wertheim and DNE Buchanan, Phys. Rev. B **50** 11070 (1994)



- Noble and alkali metals may be used to dope bulk fullerene crystal (fullerite).



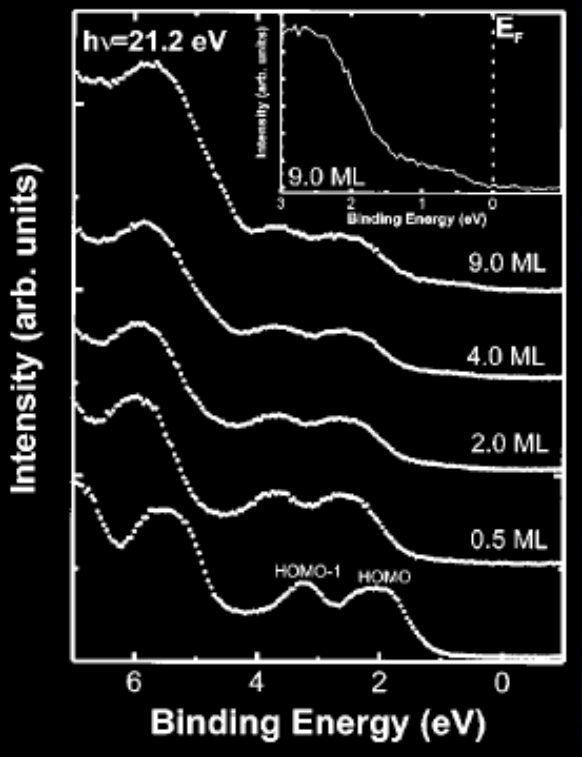
Can we tune the electronic properties of fullerene nanostructures on Si?

Taylor et al., Appl. Phys. Lett. **77** 1144 (2000)

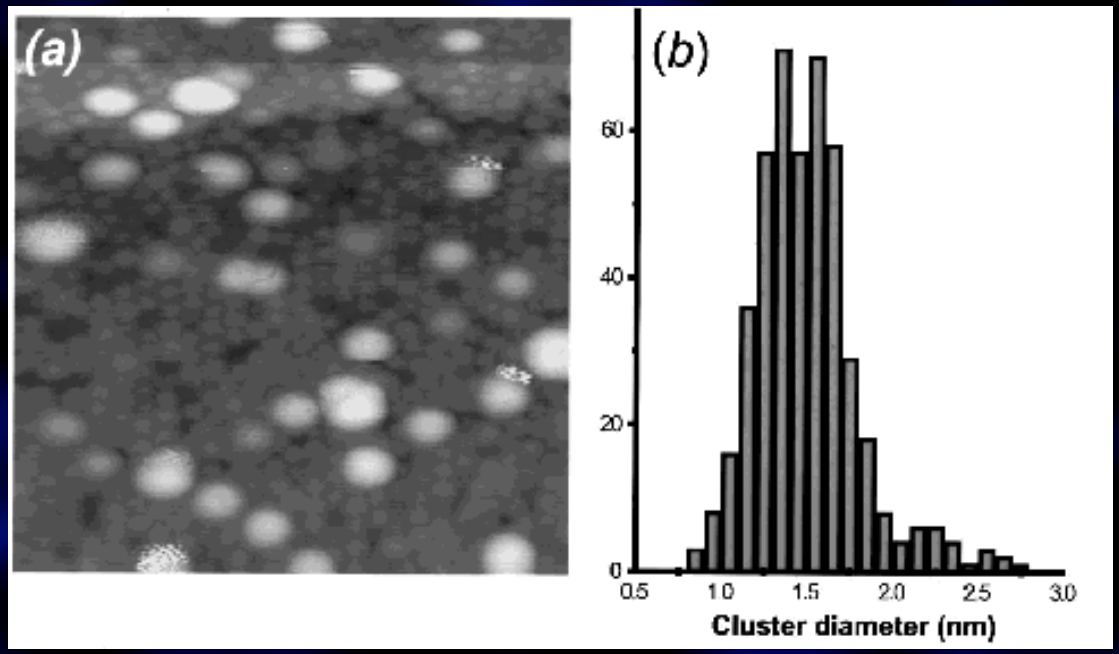
- Possible to dope bulk C_{60} with alkali and noble metals. Can we similarly dope adsorbed fullerene layers and nanostructures?

- Are conducting fullerene ‘nanowires’ a possibility?

Appl. Phys. Lett., Vol. 77, No. 8, 21 August 2000

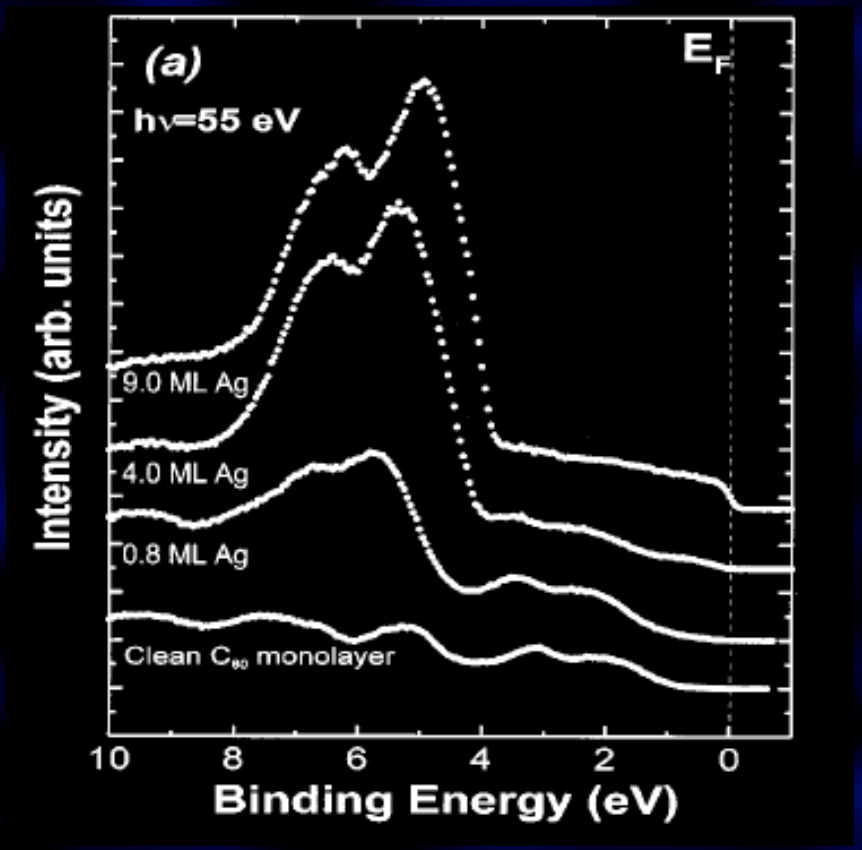


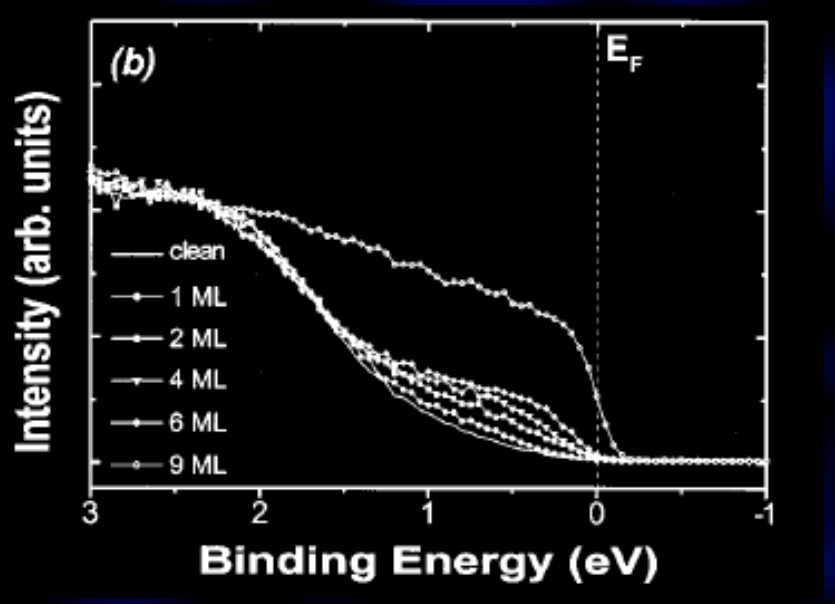
Fullerene monolayers as templates for nanoscale clusters



- Ag forms nanoscale clusters on C_{60} monolayer – narrow size distribution.
- Not observed for Au: Au deposition leads to Au silicide formation (JN O'Shea et al, J. Chem. Phys. (2003))

BE shifts of Ag-related spectral features

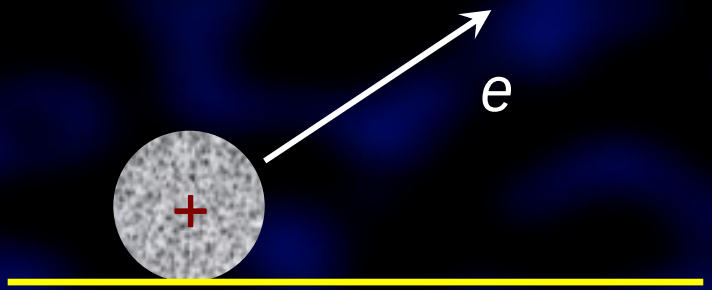




Fermi edge and Ag 4d band shift to lower BE as a function of coverage. Why?

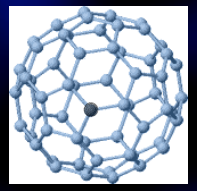
Coulomb charging of nanoscale clusters

- Cluster is isolated from fullerene ML (small amount of doping)

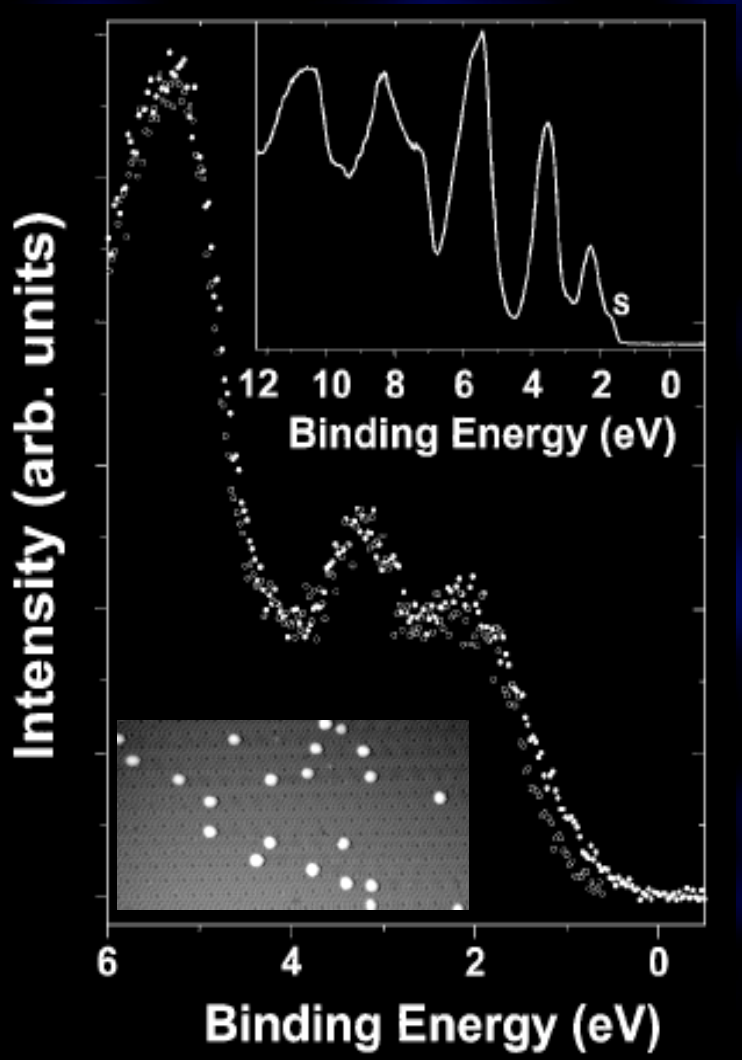


- Positive charge not neutralised on time scale of photoemission process

- Coulomb potential due to cluster charge, shifts BE by amount, $\Delta BE = e^2/8\pi\varepsilon_0 r$ (= 0.96 eV)
- Very simple model gives reasonable agreement with experimental BE shift of 0.75 (± 0.05) eV.
- Won't have 'perfect' agreement – image charges, deviations from spherical symmetry, tip convolution



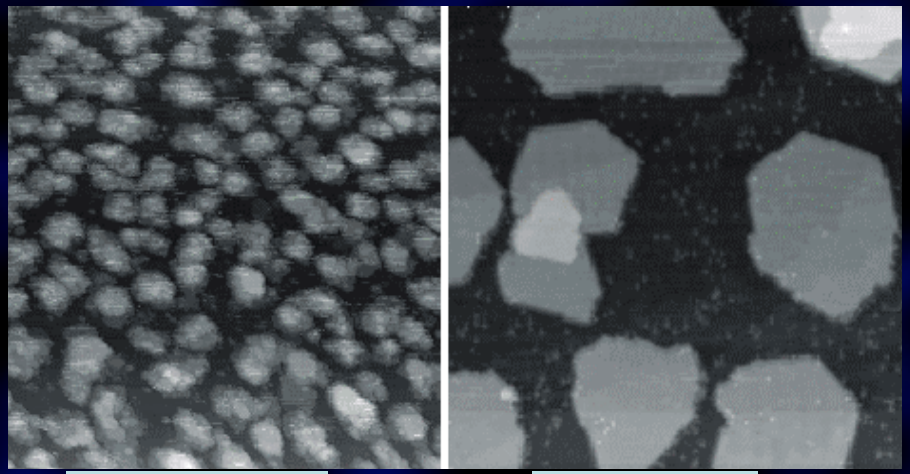
Substitutionally doped fullerenes: $C_{59}N$



- In bulk, $C_{59}N$ dimerises to form $(C_{59}N)_2$. Bulk valence band has clear signature of dimerisation (HOMO localised on dimer bond (Pichler et al PRL **78** 4249 (1997)).
- Very minor differences between VB spectra for C_{60} and $C_{59}N$ monolayers on Si.
- Manipulation properties of $C_{59}N$ very similar to those of C_{60}

Butcher et al., Phys. Rev. Lett. **83** 3478 (1999)

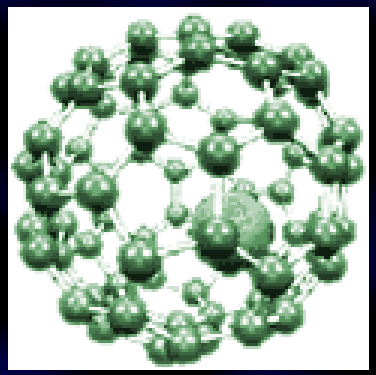
$C_{59}N$ vs C_{60}: monolayer growth on H:Si(100)



1 ML $C_{59}N$ | 1 ML C_{60}

- For deposition on clean Si surfaces, covalent bonding limits molecular diffusion
- On H:Si(100), much weaker, predominantly van der Waals interaction

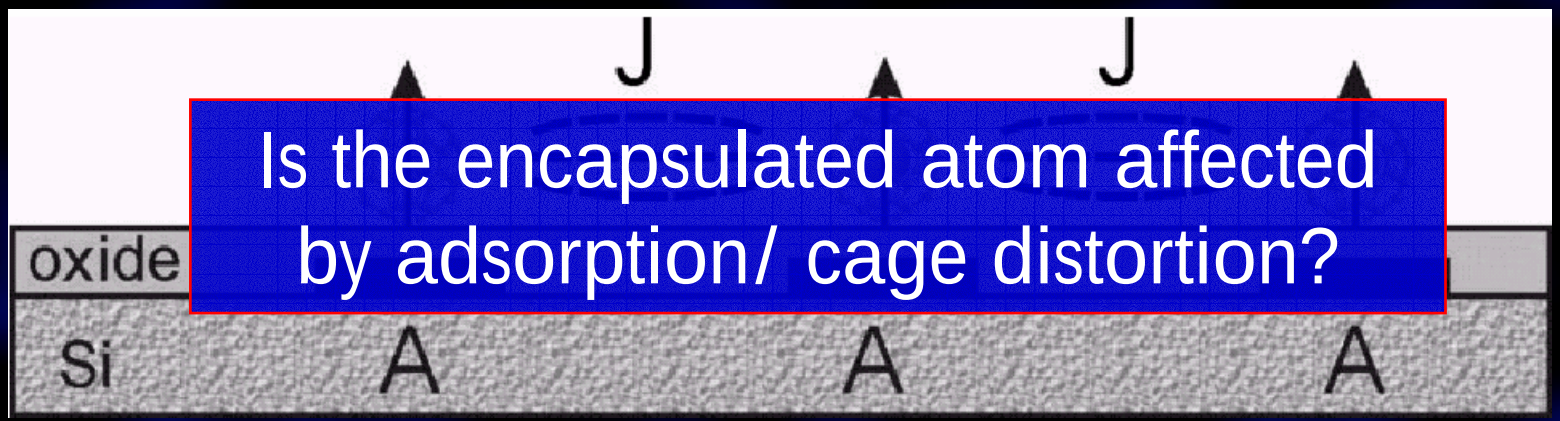
- Much higher density of $C_{59}N$ islands, not obviously faceted, much smaller.
- Differences in morphology arise because detachment rate of $C_{59}N$ molecules (E_B ~0.8 eV) much slower than that of C_{60} molecules (E_B ~ 0.28 eV). (Monte Carlo simulations, S. Balfe and D. Noble (undergraduate project 01/02) yield good agreement with experiment *if* both initial and final environments of hopping molecule taking into consideration – i.e. edge effects explicitly considered)



Endohedral fullerenes: caged atoms

Wide variety of fundamental and applied questions:

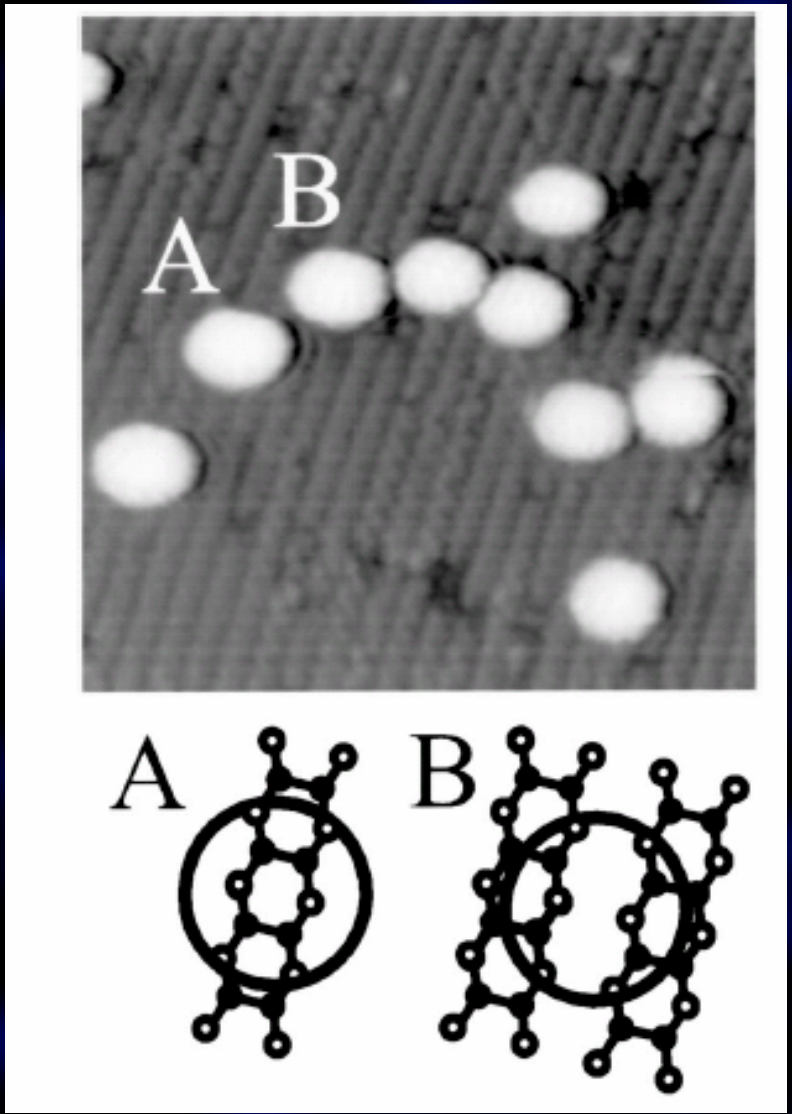
- coupling of molecular and atomic states;
- valence of encapsulated atom;
- role of encapsulated atom in adsorption/ manipulation;
- endofullerenes as qu-bits…..?

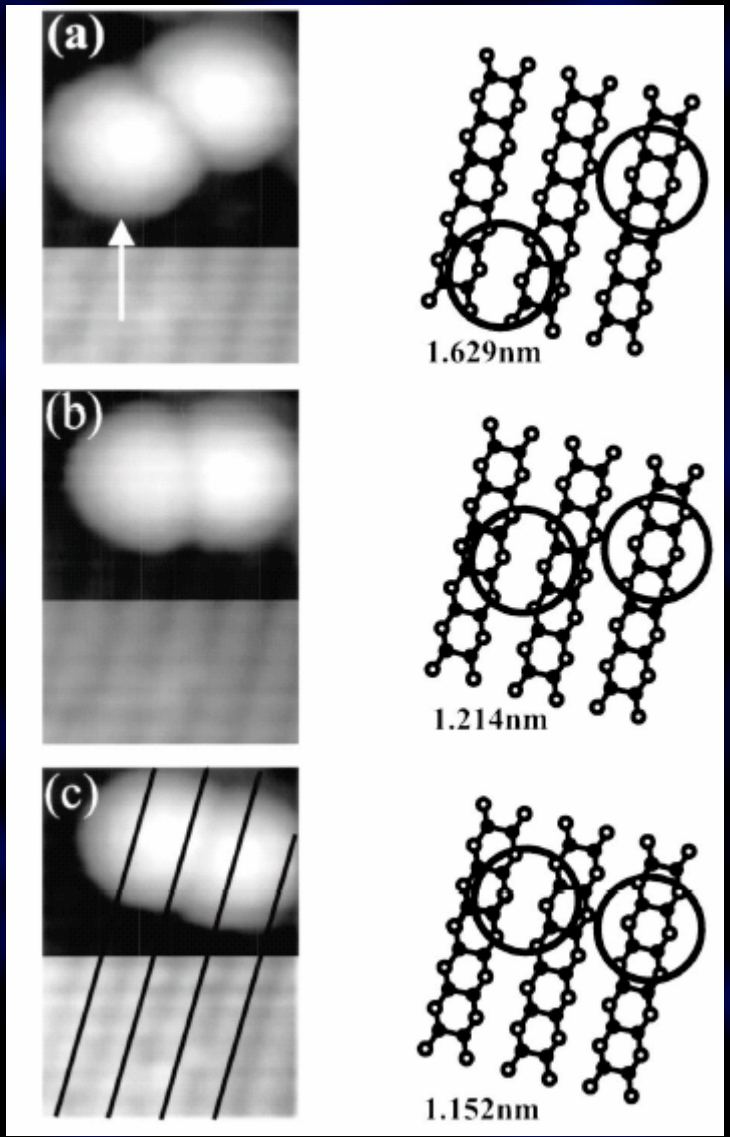


Is the encapsulated atom affected by adsorption/ cage distortion?

QIPD-DF: * W. Harneit, PRA **65**, 032322, (2002)

Imaging and manipulation of endofullerenes: La@C_{82}





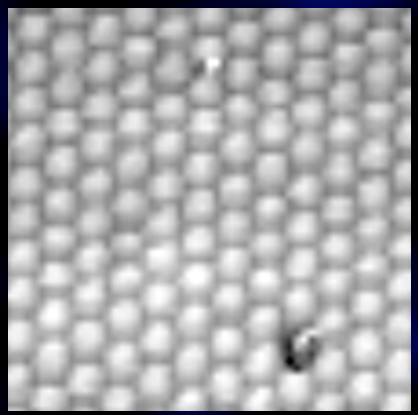
QIPD-DF: Butcher et al., PRB **67** 125413 (2003)

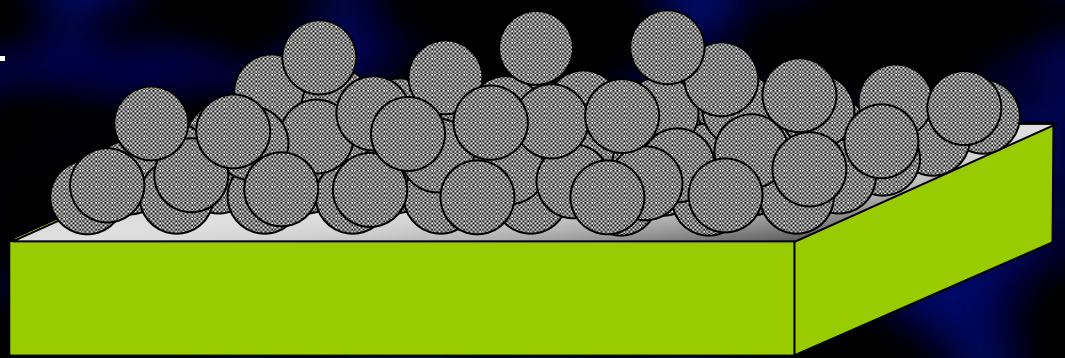
Endohedral fullerenes: experimental considerations

Difficult to deposit endofullerenes – flux decreases with total annealing time (polymerisation?).

For synchrotron measurements we have adopted the following approach:

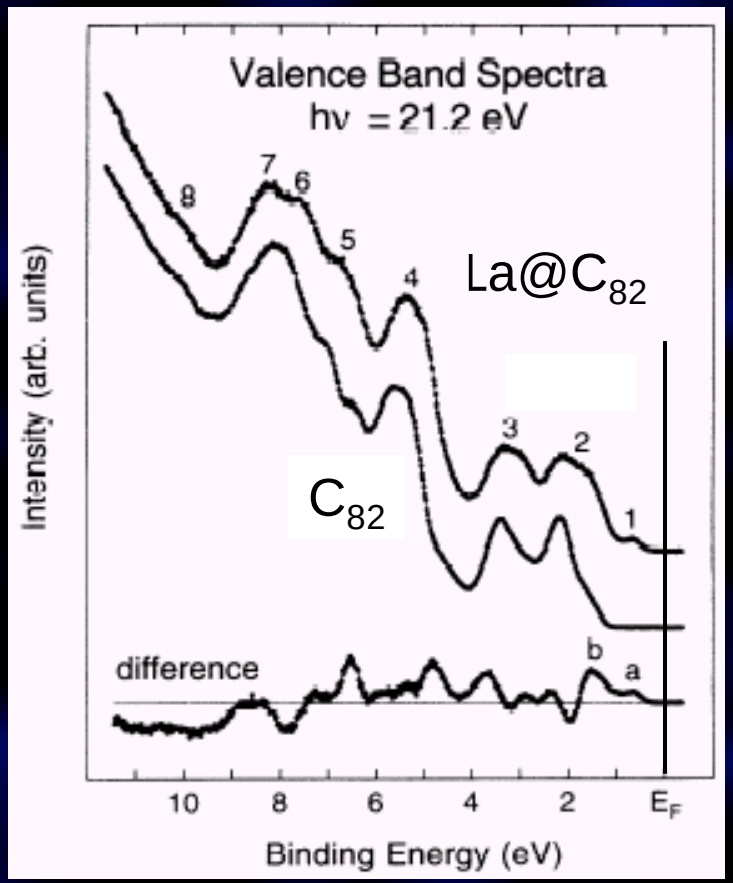
- Prepare Si(111)-(7x7) surface
- Form (passivated) Ag:Si(111)-($\sqrt{3}$ x $\sqrt{3}$)R30°
- Deposit thick film of $Ce@C_{82}$ at ~ 550 ^{o}C
- Anneal to get single covalently-bound monolayer on Si(111)

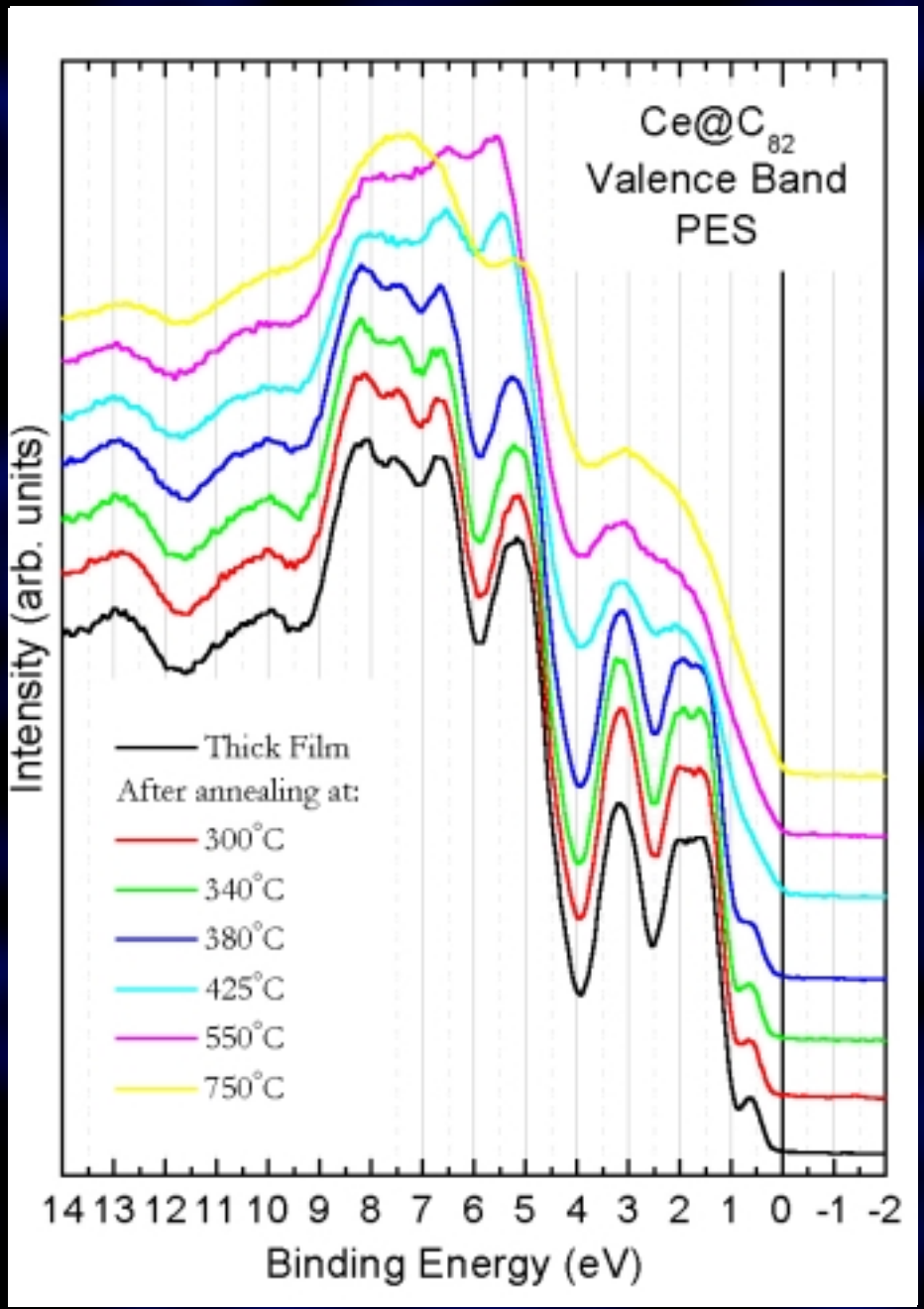




PES

Ce@C_{82} on Ag/Si(111)
Valence Band
Taken at 60 eV





D. M. Poirier *et al*., PRB **49**, 17403, (1994)

RESPES

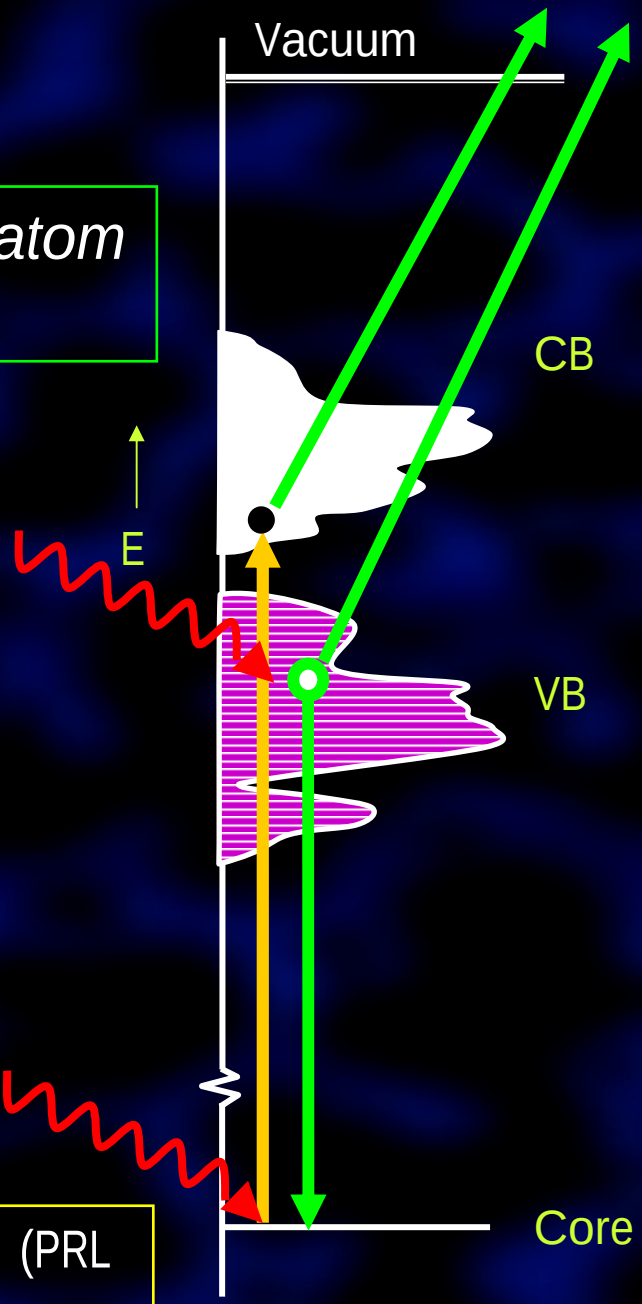
..but what contribution does the Ce atom make to the frontier orbitals?

Use *resonant photoemission* to enhance contribution (partial density of states) of Ce atom.

Interference of two processes having identical initial and final states:

(i) Participator decay (autoionisation)

(ii) Conventional photoemission

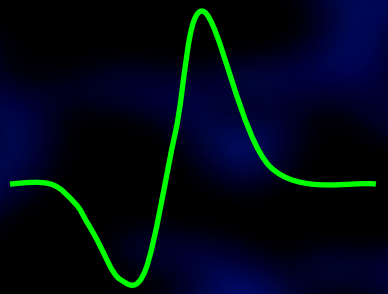


Resonant photoemission also applied by Kessler et al. (PRL 79 2289 (1997)) to bulk films of La@C_{82}.

RESPES

Two pathways interfere giving rise to large variation in photoionisation cross-section across threshold: *Fano* resonance.

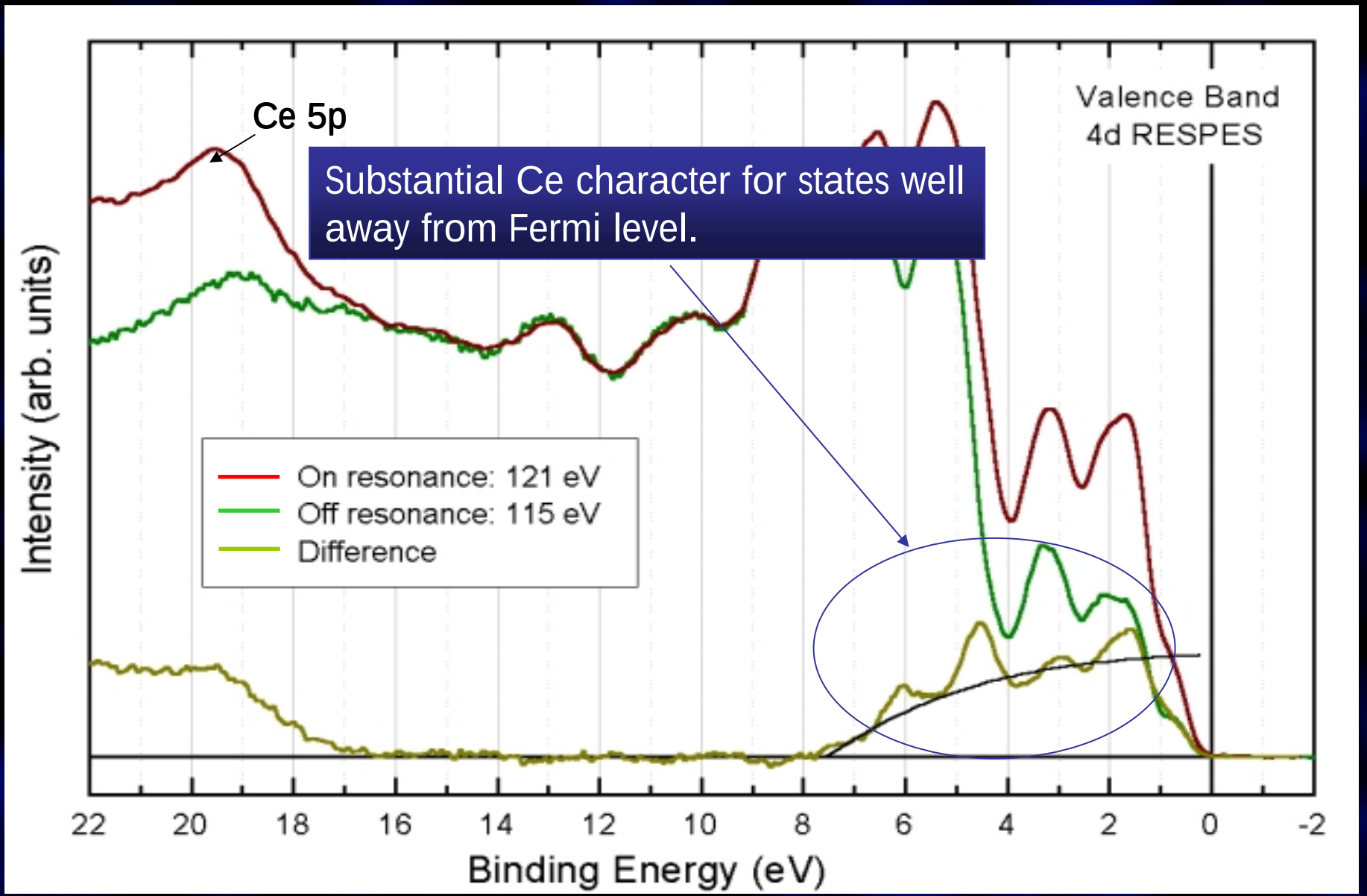
Importantly, RESPES is a *site-specific* probe (provided only intra-atomic decay takes place during the autoionisation process).



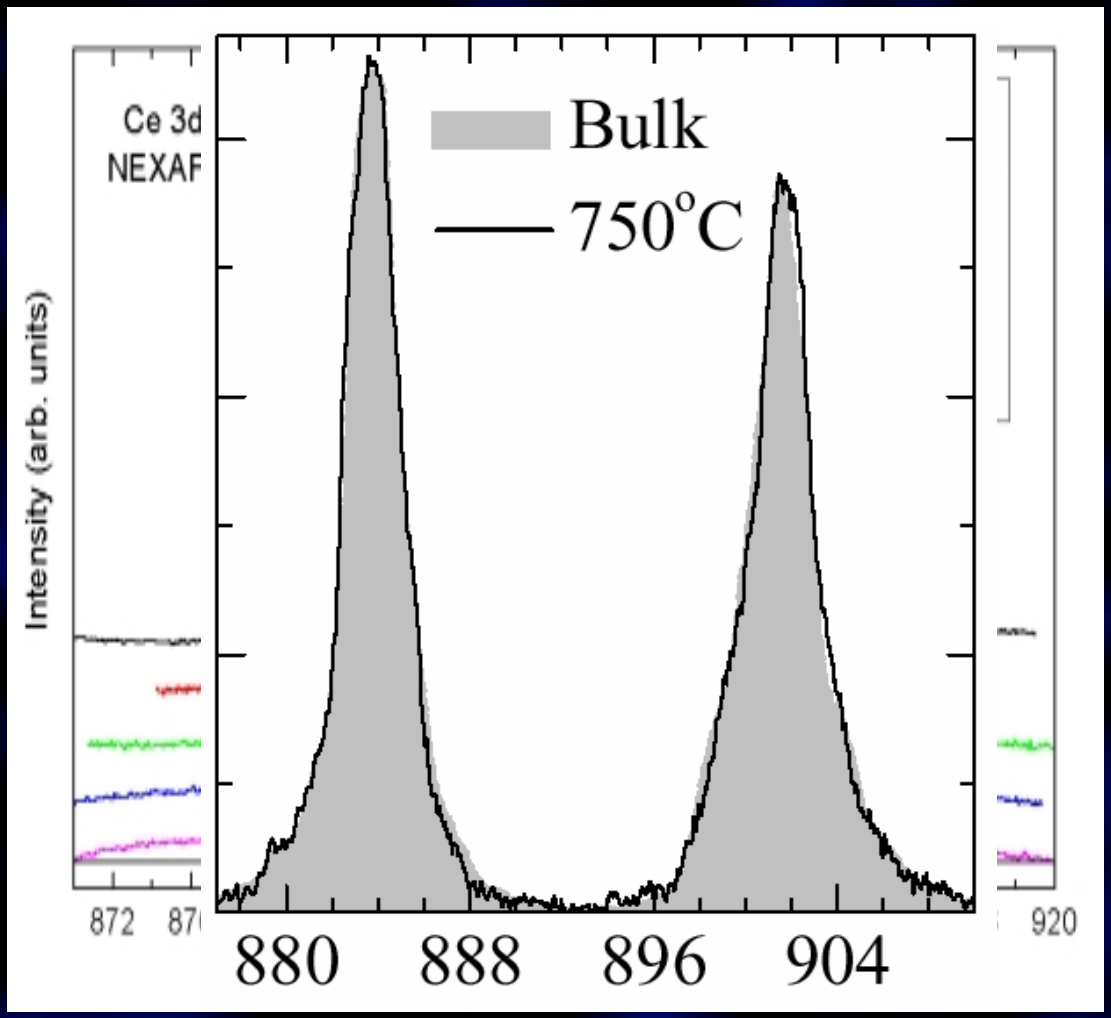
Large number of RESPES studies of 4f spectral weights in various Ce compounds.

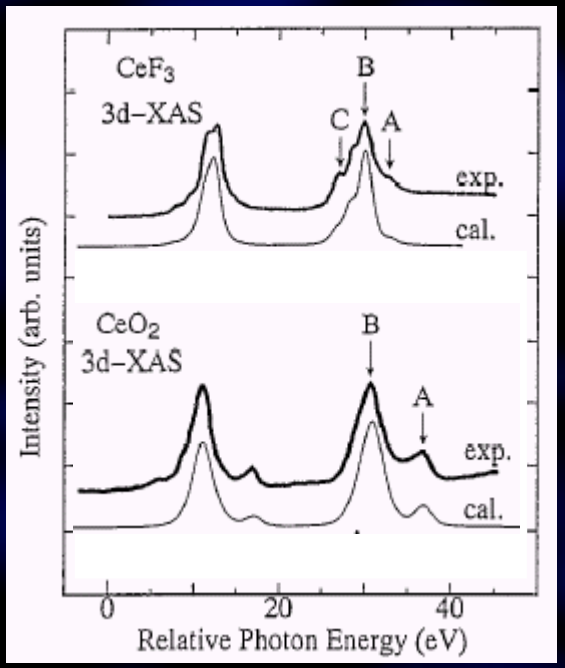
$$4d^{10}4f^{1} + h\nu \rightarrow 4d^{9}4f^{2} \rightarrow 4d^{10}4f^{0} + \text{photoelectron}$$

Ce 4d RESPES


Ce 5p
Substantial Ce character for states well away from Fermi level.
Valence Band
4d RESPES
On resonance: 121 eV
Off resonance: 115 eV
Difference
Intensity (arb. units)
22
20
18
16
14
12
10
8
6
4
2
0
-2
Binding Energy (eV)

Ce 3d NEXAFS



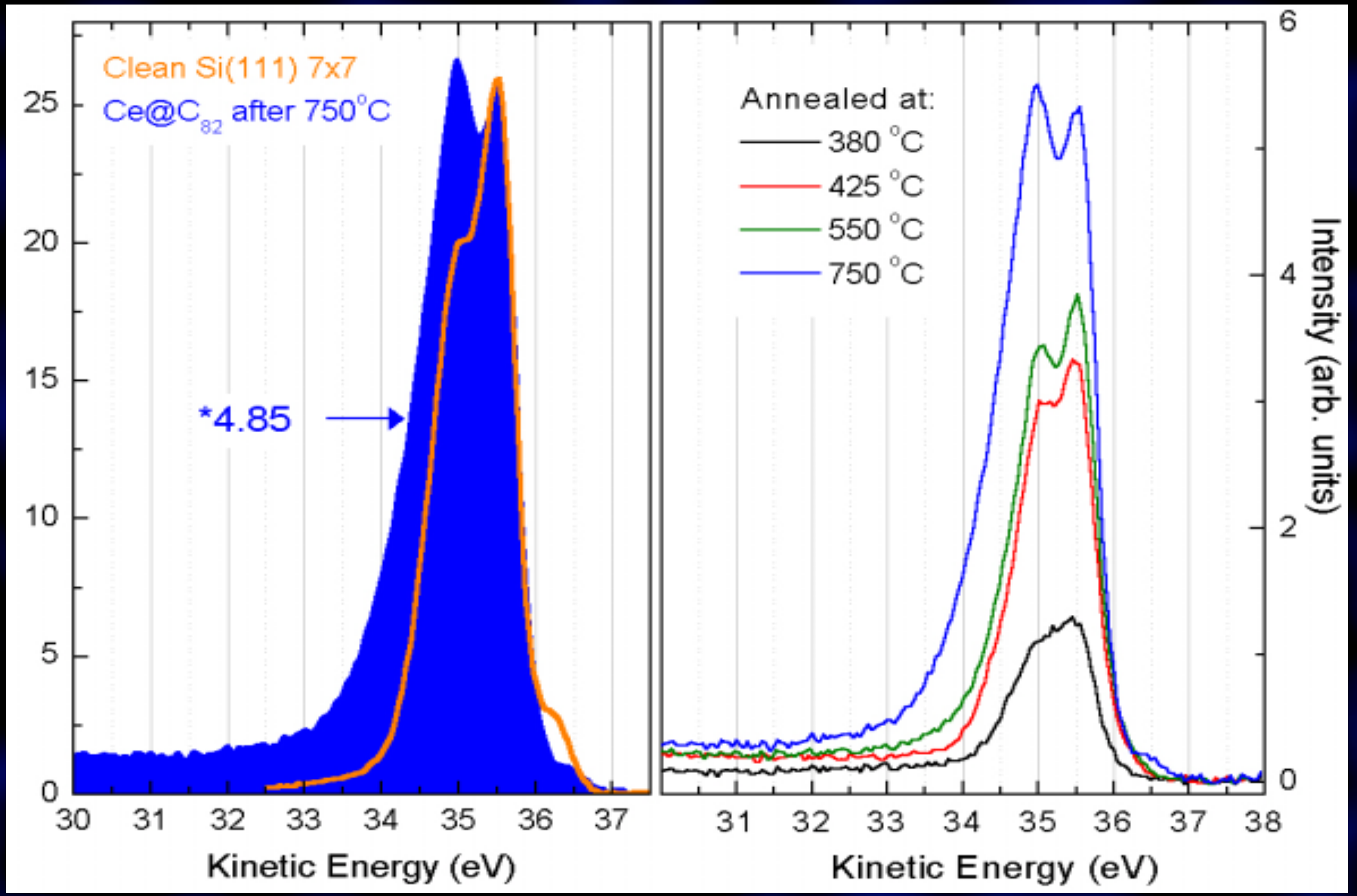


M. Nakazawa et al., J. El. Spec. Rel. Phen. **79** 183 (1996)

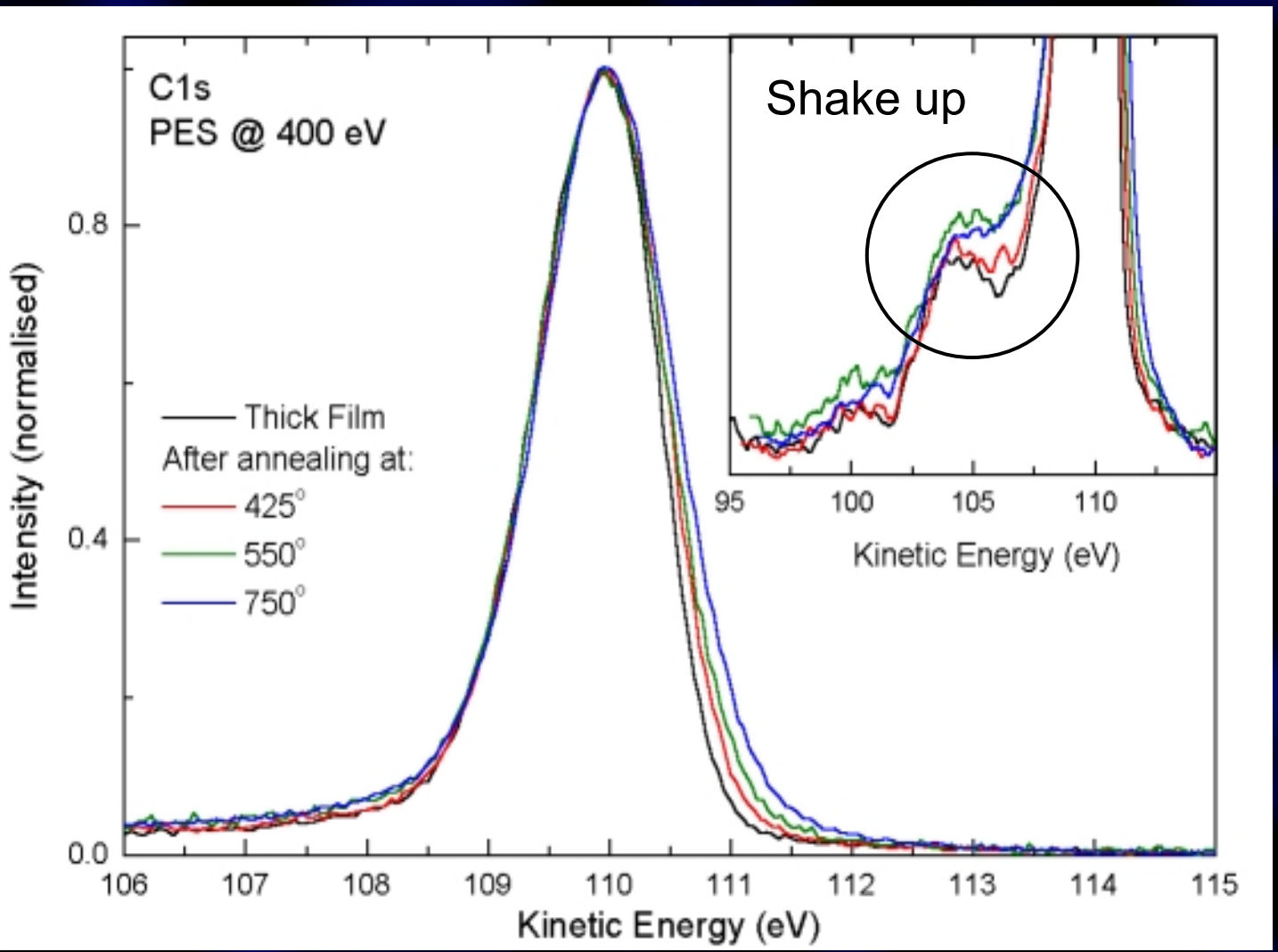
Ce in close to *3+* oxidation state – **negligible** change in NEXAFS spectrum as surface-molecule interaction increases.

[Schulte et al., submitted to Phys. Rev. B]

Si 2p PES: Si-C covalent bonding



C 1s PES



FWHM:

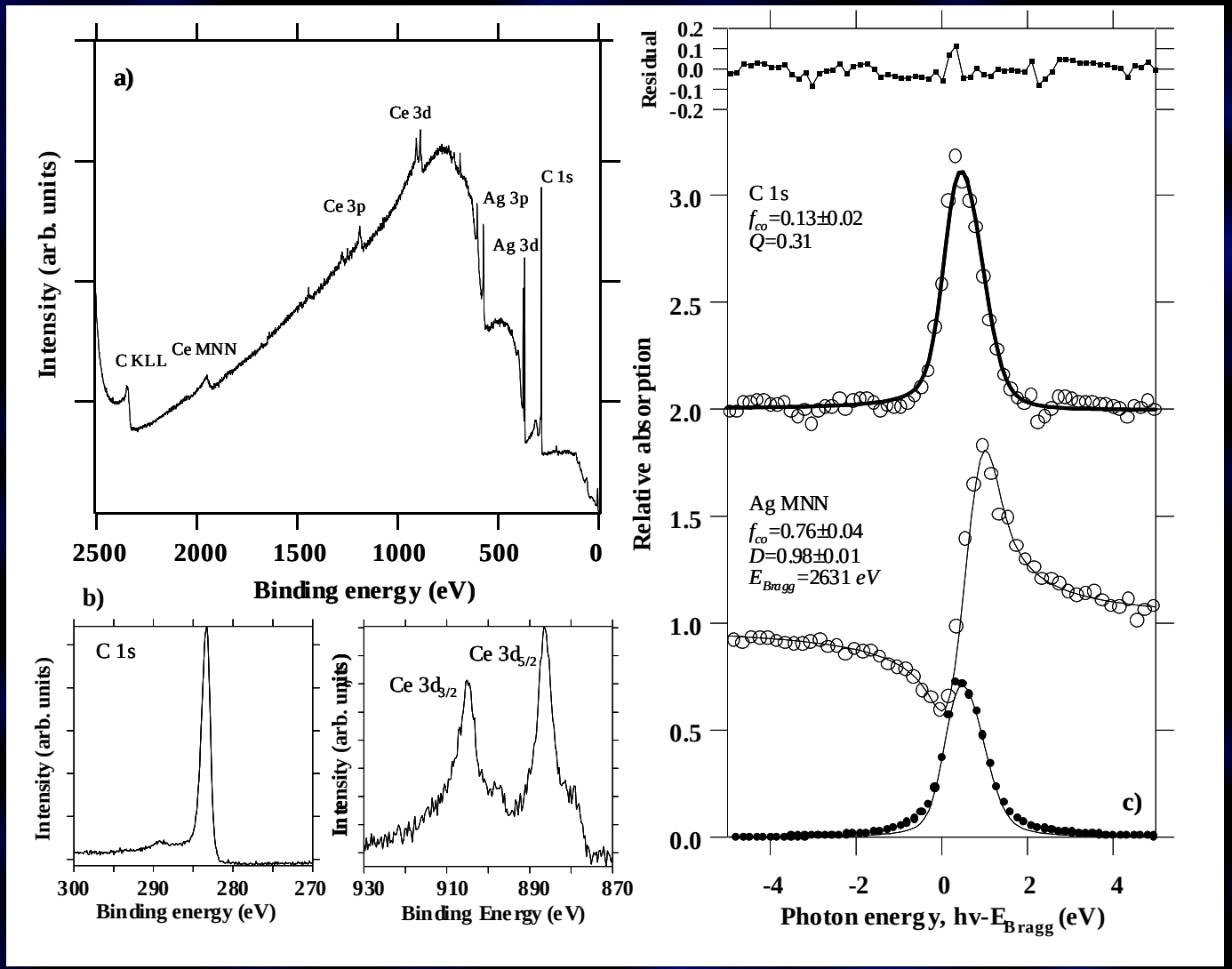
- Thick Film 1.16 eV
- After 750 °C 1.32 eV

Shake up structure still present at high temperatures: cage remains intact.

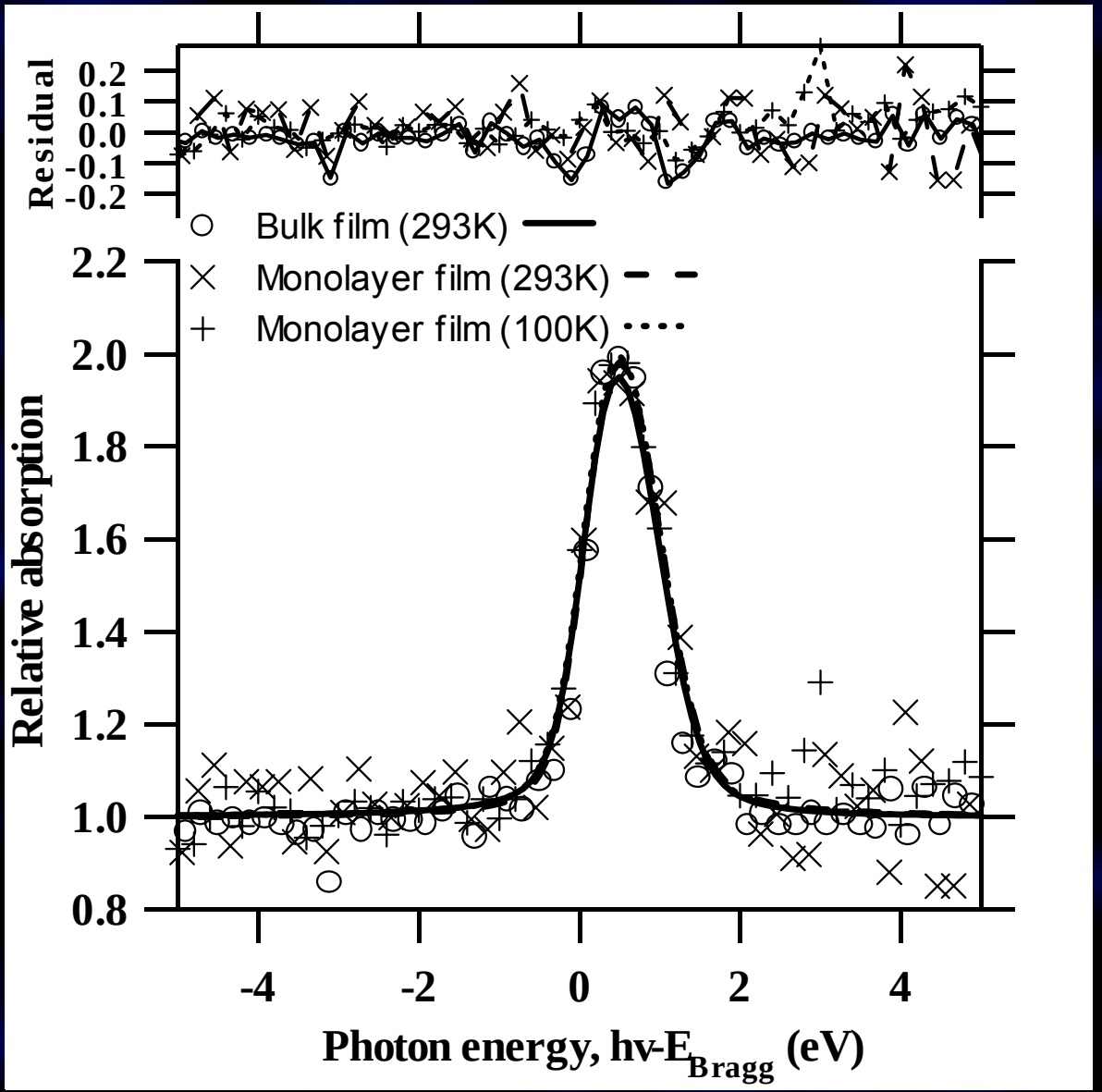
Probing the position of the incarcerated atom: XSW

$$Y_P = 1 + R + 2\sqrt{R}\, f_{co} \cos(\phi - 2\pi D)$$

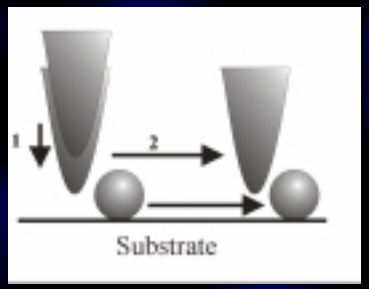
RAJ Woolley et al., Nano Lett. (2004)



Probing the position of the incarcerated atom: XSW

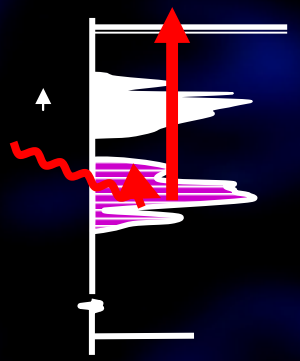


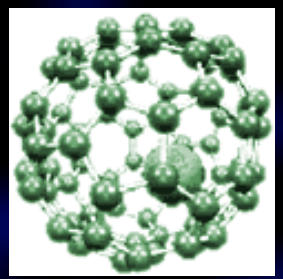
Conclusions



Endofullerenes may be manipulated with sub-nanometre precision on Si surfaces.

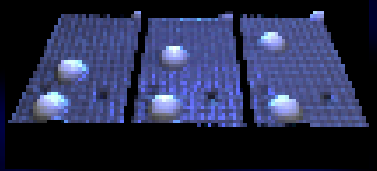
SR-based spectroscopies provide a wealth of information on fullerene-silicon interactions: covalency, charge transfer and doping, (..electron correlation..).

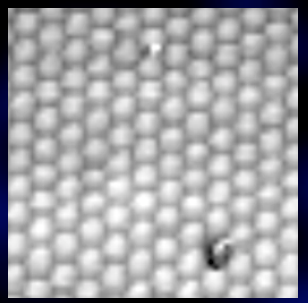


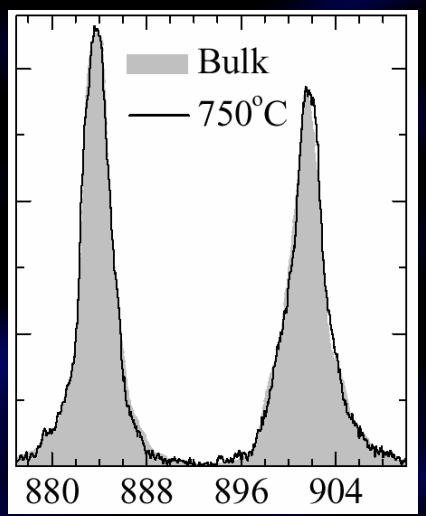


In $Ce@C_{82}$ (and other rare earth endofullerenes) there is a strong lanthanide-cage interaction. Systematic study of endofullerene-surface interactions shows that even in the presence of strong Si-C bonds, encapsulated atom is rather weakly perturbed.

….what's next?: projects within NANOCAGE







- Tunnelling spectroscopy: *I(z)*, *I(V)*, *dI/dV*, d^2I/dV^2
  - Role of encapsulated atom
  - Compression (compare to C_{82})
  - Distinguish C_{82} from $Ce@C_{82}$ via vibrational spectroscopy? [Difficult – lack of symmetry…?]
  - Manipulation – track forces using AFM.
  - DFT: electronic structure, transport…

- $N@C_{60}$
  - How do we form a monolayer/ thin film?
  - XSW – multilayers – locate atom in molecule – 'track' as it leaves cage.
  - Excited state decay – lack of coupling of N to cage should produce very long lived excited state. (Overlap of excited state with cage orbitals?)

Peapods