Size-Selective Carbon Nanoclusters as Precursors to the Growth of Epitaxial Graphene

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Combination of STM and DFT to study the growth of graphene from ethylene CVD on Rh(111)

Work published in: B. Wang *et al*., Nano Letters **11**, 424-430 (2011)

Outline

- What we know (and don't know) about graphene formation on TM surfaces
- Ethylene/Rh(111): temperature programmed growth (TPG)
- Identification of size-selective carbon clusters as precursors: C_{24}
- Comparison with $C_{24}H_{12}$/Rh(111)
- Understanding the "magic" stability of C_{24} from first-principles

How does graphene form on 4*d* & 5*d* TMs?

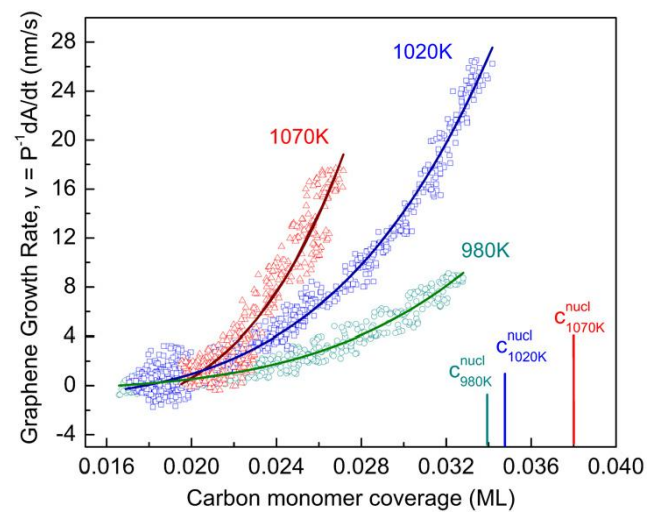
- We don't know what are the processes that bring carbidic clusters (strongly bound) to develop into a graphene island (weakly bound)

- Graphene/TM by DFT (from Peter Feibelman's work):
  - attachment energy of isolated C atom to graphene edge **is prohibitively high**, whereas it decreases significantly for larger C clusters

- Graphene/Ru(0001) by LEEM (from Kevin McCarty's work):
  - non-linear growth kinetics strongly suggests growth by incorporation of clusters of **approximately 5 C** atoms rather than monomers

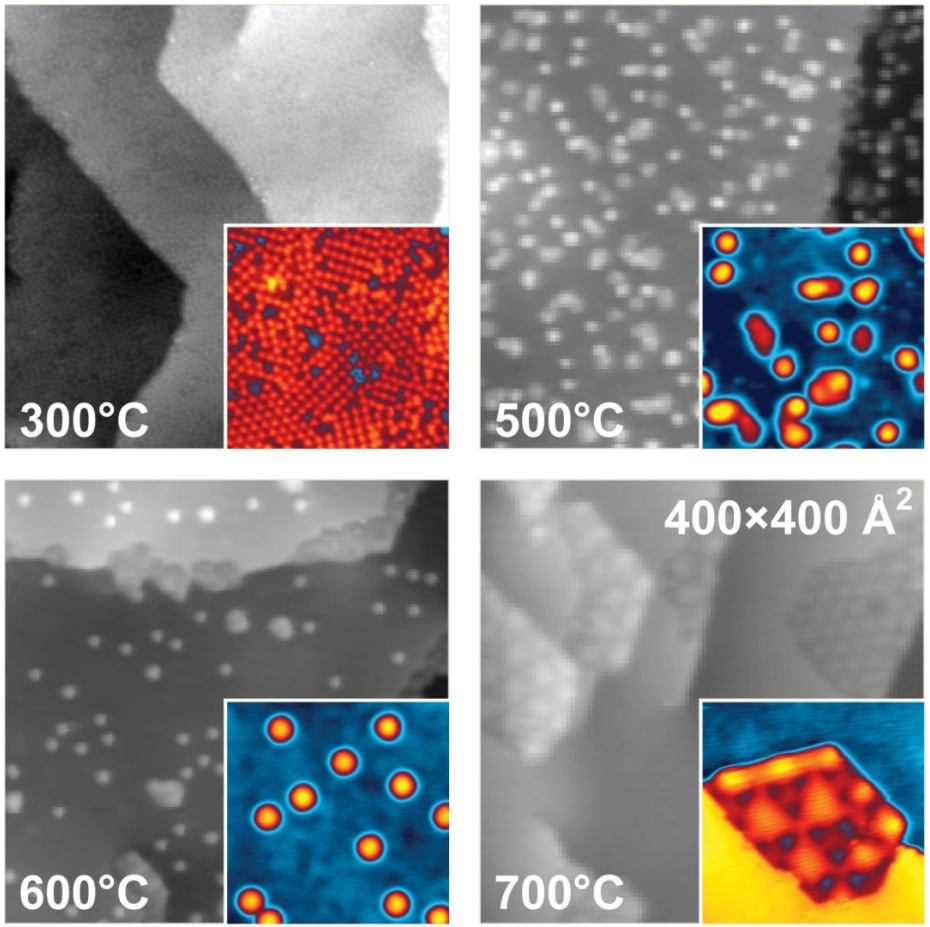
- Yet, these fundamental building blocks of graphene have not been formally identified

- We will perform TPG of ethylene on Rh(111)



Loginova *et al.*, NJP **10**, 093026 (2008)

Morphology evolution during TPG: 18 L of C_2H_4 at RT on Rh(111)



- At 300°C:
  - (2×2) and c(4×2) superstructures
  - ethene deprotonates to ethylidyne
  - adsorbs in 3-fold hcp hollow sites
  - C-C axis normal to the surface
- At 500°C:
  - small protrusions located on terraces
  - sizes from ranging from 1 to 2 nm
  - apparent height of less than 0.2 nm
- At 600°C and above:
  - single cluster size of 1 nm
  - decrease in the particle density
  - emergence of graphene islands

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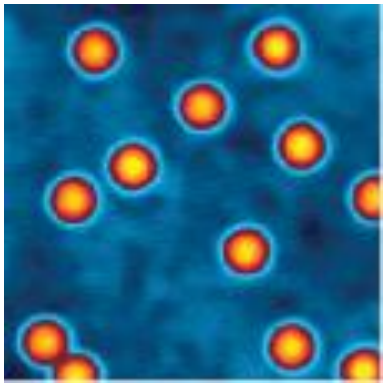

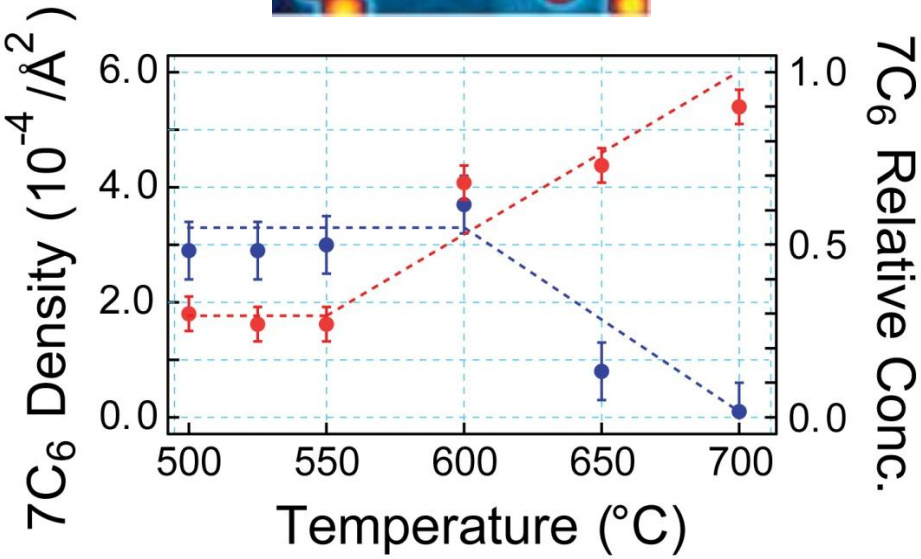

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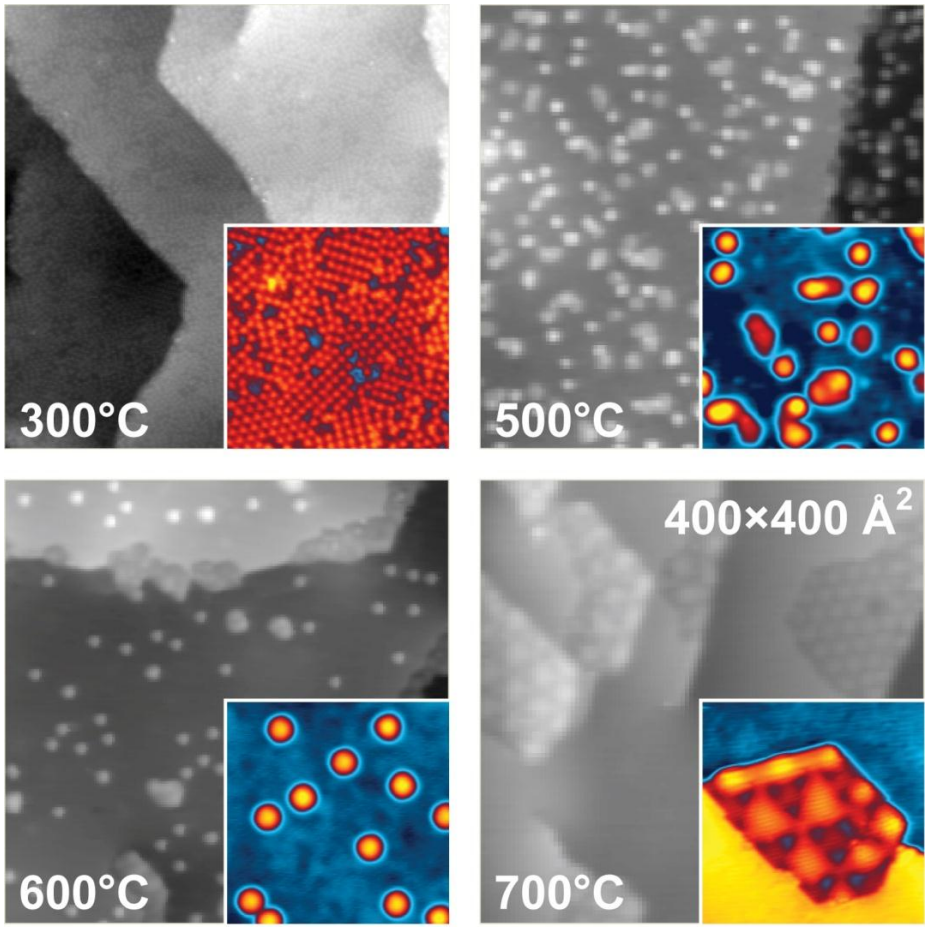
Size-selective carbon nano-islands as precursors to graphene !

Growth mechanism: Smoluchowski ripening

- RT: adsorbed ethene → ethylidyne



- Annealing → thermal decomposition
  - structural rearrangement of C-C bonds → C2 coupling
  - dehydrogenation (C-H bond scission, H evolution)
  - in line with C_2H_4/Pt(111)

    Land *et al*. Surf. Sci. **264**, 261 (1992)

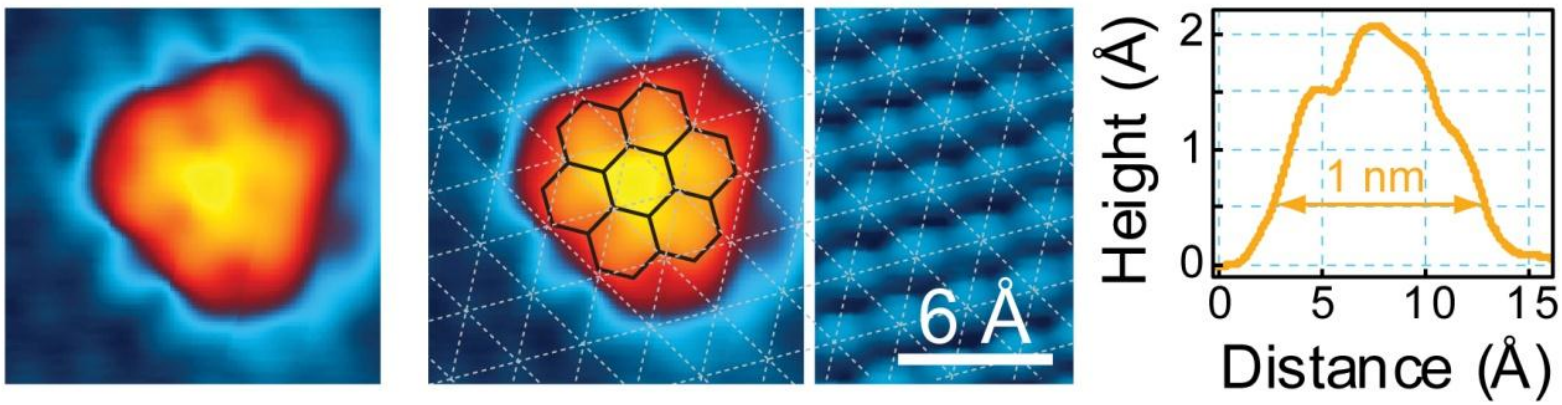
- Remarkable:
  - evolution to mono-dispersed entity
  - randomly scattered on terraces
  - no influence of step edges
  - no loss of carbon to the bulk

- Decrease in mono-dispersed clusters → graphene growth
  - not only at steps but also on terraces

- Rate determining step in graphene growth: cluster coalescence mechanism

Identification of the magic carbon clusters

- Size distribution of the carbon clusters at different temperatures reveals lower limit, or critical size:
  - diameter of 1 nm
  - nearly perfectly hexagonal in shape and adsorbed in 3-fold fcc hollow site



- thermal decomposition (dehydrogenation) of ethene is complete above 770 K:
  - most probable chemical structure: 7 honeycomb carbon units arranged in hexagon
  - from STM images at low bias: visual impression that central benzene unit lies higher than its surrounding neighbours → 2 Å high dome-shaped configuration

→ **$7C_6$**

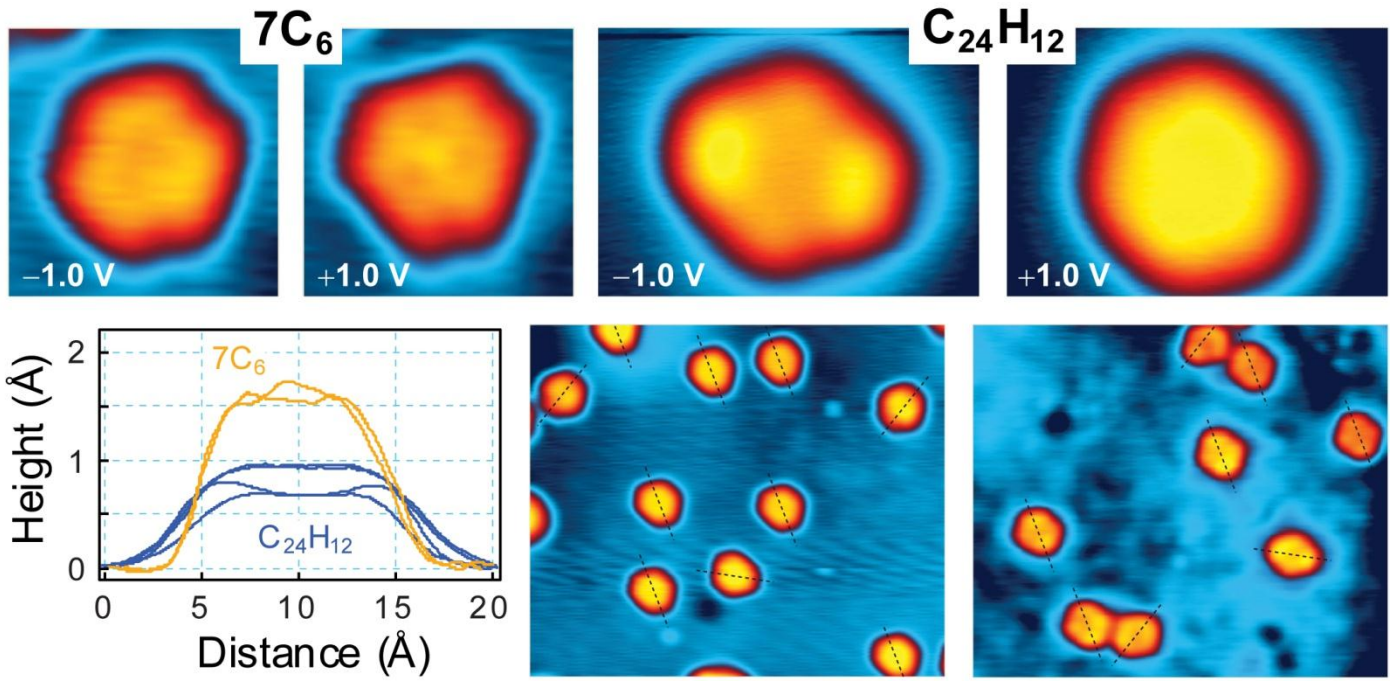
How can we prove it?

1) Comparison with coronene
2) STS for electronic fingerprint
3) DFT support

$7C_6$ vs. coronene: topography

- Coronene = $C_{24}H_{12}$ = the hydrogenated analogue of $7C_6$

- Coronene deposited at RT on Rh(111):



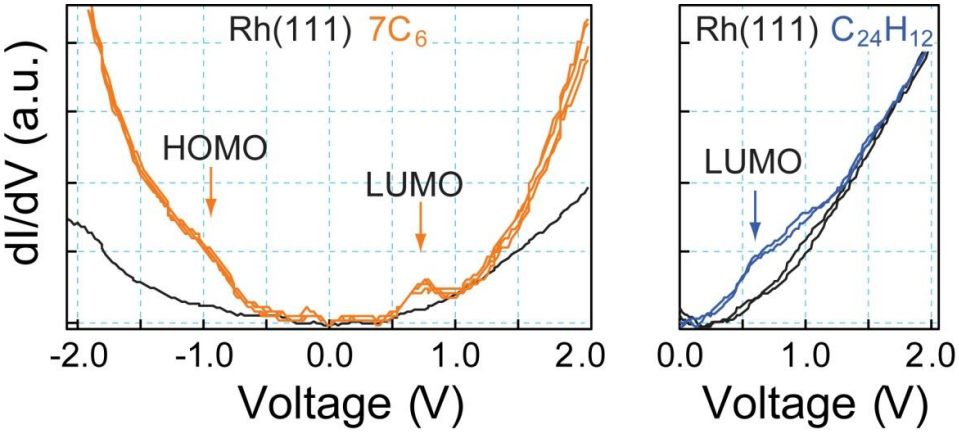
- STM topographic images show (irrespective of tunnelling bias):
  - lateral size: $C_{24}H_{12}$ **>** $7C_6$ in line with molecular skeleton
  - electronic height : $C_{24}H_{12}$ **<** $7C_6$ by 0.5 Å
  - symmetry: 2-fold ; 3-fold different adsorption sites

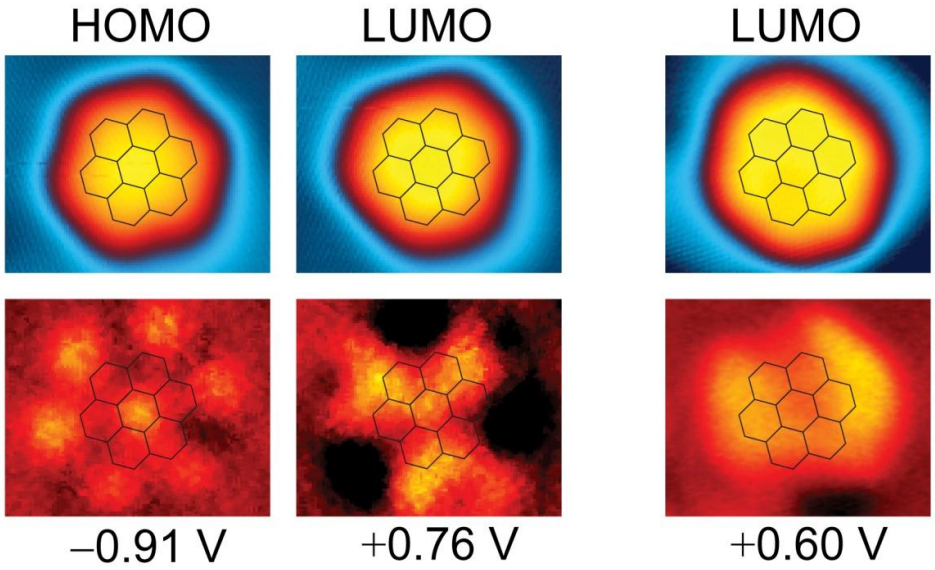
$7C_6$ vs. coronene: electronic structure

- dI/dV spectra identify:
  - $7C_6$: two resonances (HO+LU-MO)
  - $C_{24}H_{12}$: single resonance (LUMO)
  - spectra are different

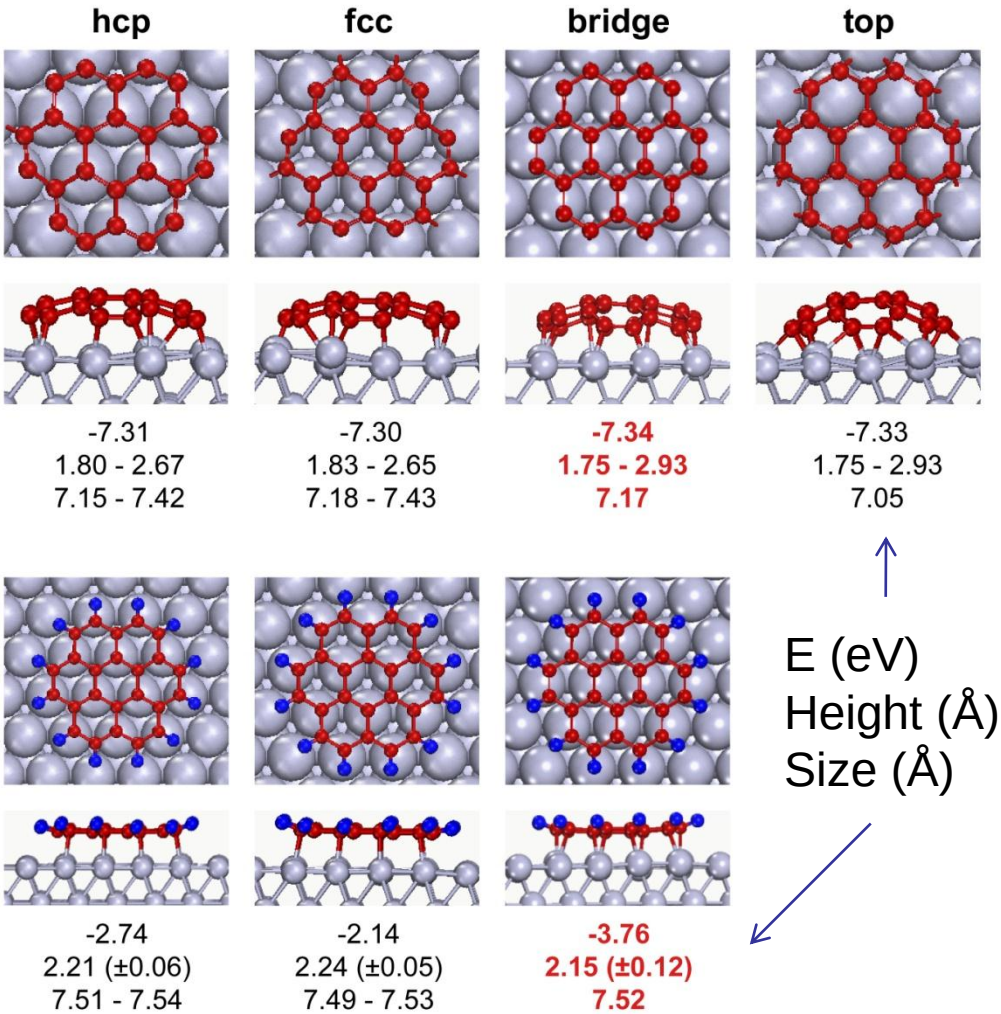
- dI/dV images at resonances:
  - $7C_6$: 3/6-fold symmetric
  - $C_{24}H_{12}$: 2-fold symmetric

- $7C_6$ and $C_{24}H_{12}$ are two different chemical entities:
  - different topographic signatures
  - different adsorption sites
  - different electronic signatures





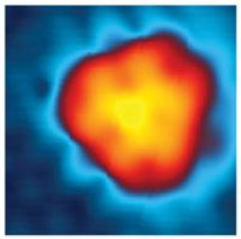
DFT optimized structures



E (eV)
Height (Å)
Size (Å)

In agreement with: Lacovig *et al*., PRL **103** (2009)

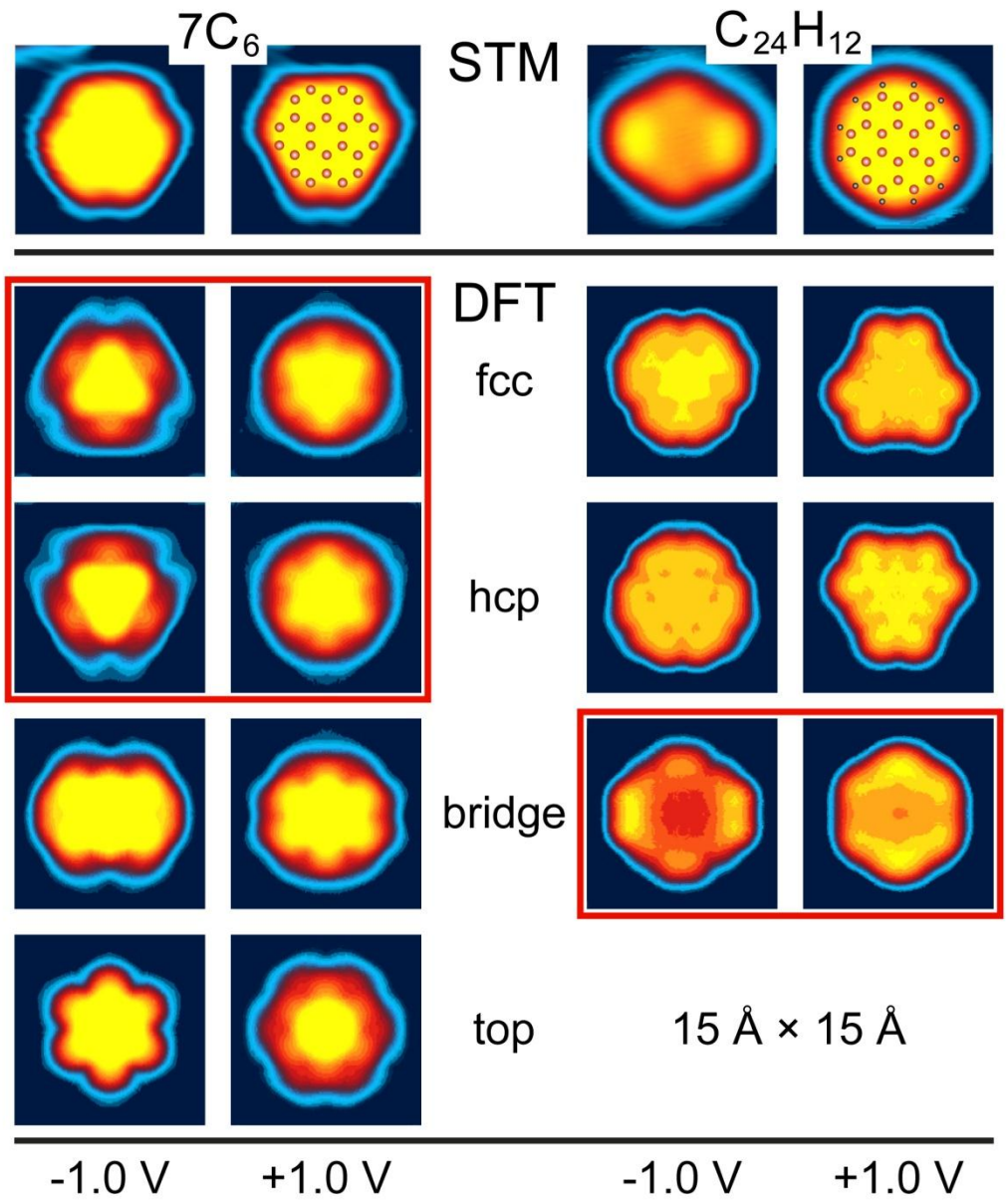
- Predictions for $7C_6$:
  - adsorbs "equally" on all registries
    → STM reveals ONLY fcc !
  - dome-shaped with central benzene unit higher
  - bonding to substrate mainly at peripheral C atoms



- Predictions for $C_{24}H_{12}$:
  - adsorption strongly favours bridge sites
  - geometric height lower than $7C_6$ by 0.5-0.8 Å
  - bonding to substrate shared by all C atoms

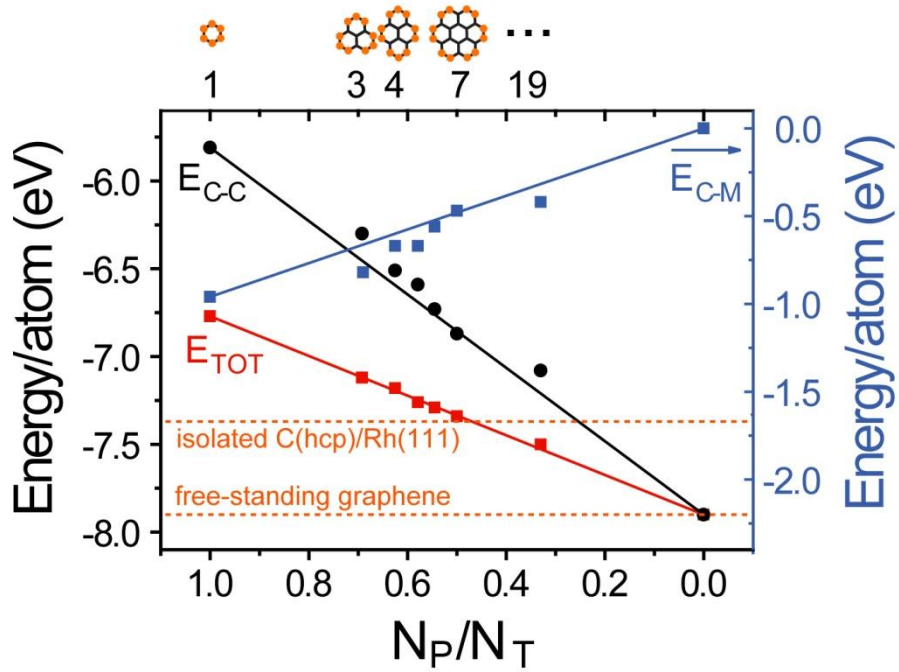
$7C_6$ vs. coronene: simulated STM images

- Simulated STM images seem to confirm that the favoured adsorption site is:
  - $7C_6$: 3-fold hollow site
  - $C_{24}H_{12}$: 2-fold bridge site



Theoretical stability of NC_6 clusters

- Computed formation energy for various carbon cluster sizes (in units of benzene rings) on Rh(111)
  - $E_{C\text{-}C}$ = formation energy, free cluster
  - $E_{C\text{-}M}$ = adsorption energy
  - E_{TOT} = overall energy gain
  - X axis = ratio edge C's / total C's

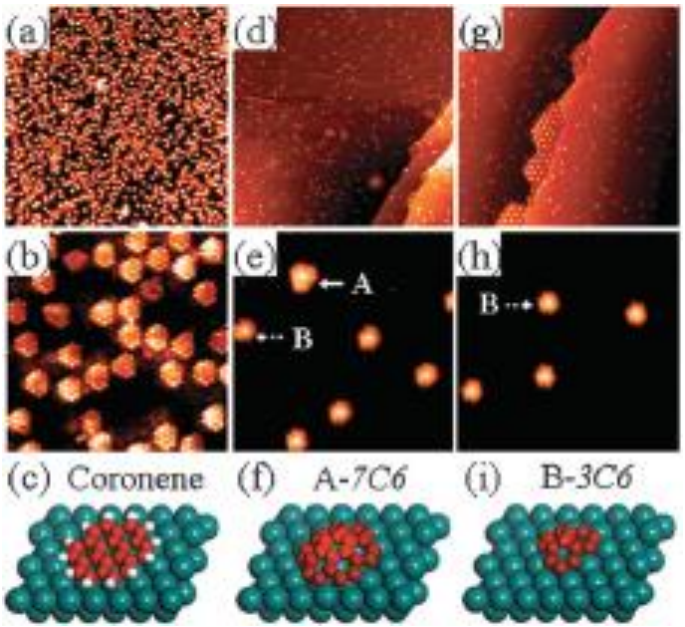


- NC_6 carbon cluster stability scales linearly with $\frac{\text{number of edge atoms}}{\text{total number of atoms}}$
  → peripheral bonding (Lacovig et al. PRL 2009)

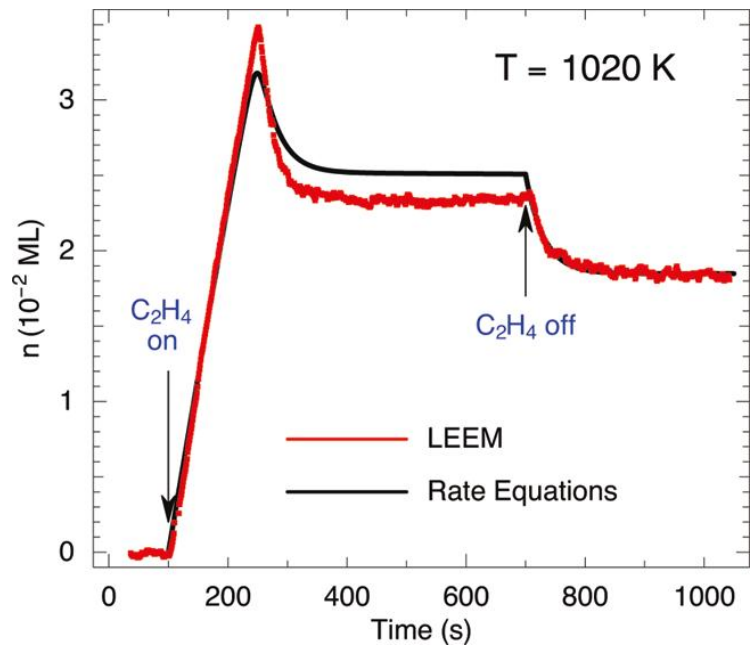
- NC_6 carbon clusters become more stable than isolated C atoms for ***N* = 7** !

- Stability arises from a delicate balance between C-C and C-M bond strengths

Is this particular to the G/Rh(111) system?



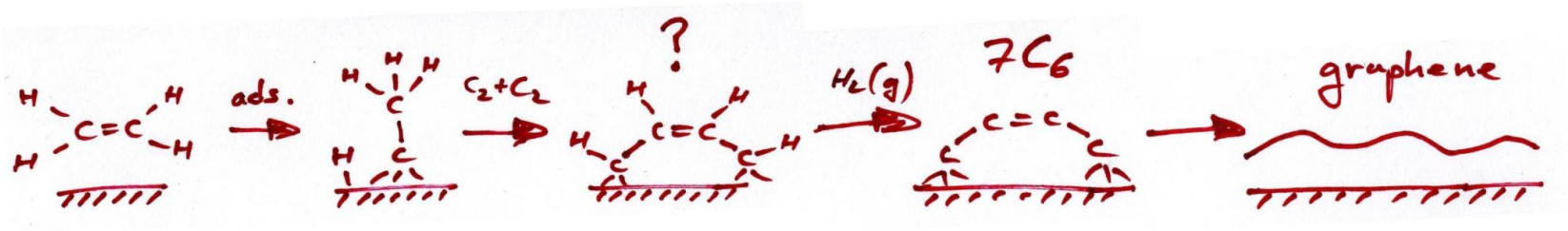
- Graphene growth on Ru(0001) also proceeds by via the formation of NC_6 precursors.
  - Ciu et al., *Chem.Comm.* **47**, 1470 (2011)



- Zangwill and Vvedensky show, on the basis of the McCarty LEEM data, that graphene islands grow by the attachment of 5C clusters, and predict that the smallest stable precursor to graphene is $6C_5$.
  - Nano Letters **11**, 2092 (2011); NJP **11**, 063046 (2009)

Take-home message

- Graphene growth on Rh(111) proceeds under TPG by:
  - adsorption of the carbon source, dehydrogenation and coupling of C_2 units;
  - stabilization of mono-dispersed carbon clusters: $7C_6$;
  - formation by incorporation, coalescence (Smoluchowski ripening).



Those who did the work

- Research group in St Andrews, UK performed STM
  - Bo Wang
  - Marco Caffio

- Collaborators in Dalian, China performed DFT
  - Prof. Wei-Xue Li
  - Xiufang Ma

- Funding
  - EaStCHEM Research School
  - Scottish Funding Council

Thanks for listening

Computational details

(Xiufang Ma, Wei-Xue Li @ Dalian, China)

- Periodic DFT calculations using VASP
  - generalized gradient approximation, PBE functional
  - PAW potentials
  - plane wave basis with 400 eV cutoff energy for geometry (electronic) calculations
  - optimization with residual forces on atoms less than 0.02 eV/Å

- Supercell
  - slab geometry composed of five metal layers with lower two kept frozen
  - vacuum region of about 15 Å,
  - for C atom adsorption: use (2×2) unit cell with (6×6×1) Monkhorst-Pack grids.
  - for C clusters: use (4×4), (6×6), (7×7) unit cell according to cluster size and use (3×3), (2×2), (1×1) Γ centered K sampling points for the BWZ.