Laboratory Investigations of the Formation of Superhydrogenated PAHs

A possible route to H_2 formation

Andrew Cassidy

(John Thrower)

Department of Physics and Astronomy, Aarhus University, Denmark

DEPARTMENT OF PHYSICS AND ASTRONOMY

FACULTY OF SCIENCE
AARHUS UNIVERSITY

iNANO

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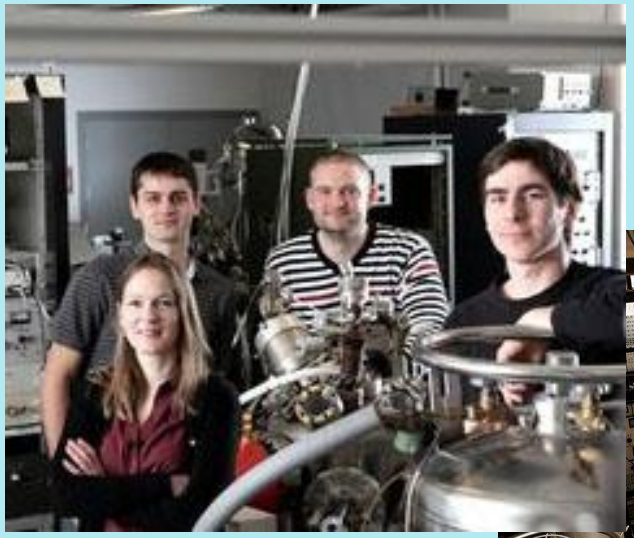
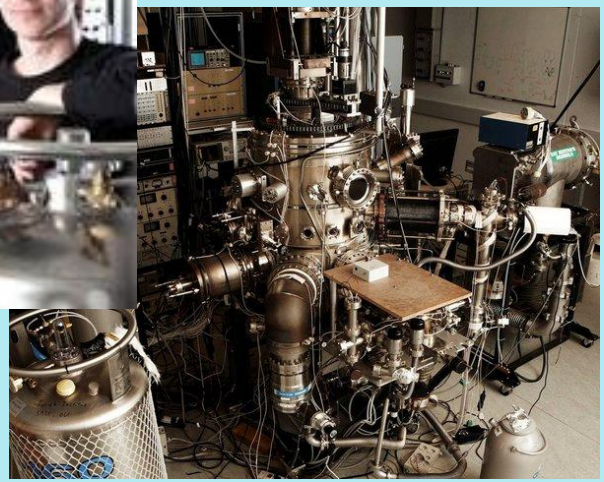
- Liv Hornekær
- Experiments
  - Richard Balog
  - Louis Nilsson
  - Bjarke Jørgensen
  - Emil Friis
  - Saoud Baouche
  - Anders Lind Skov
- DFT
  - Eva Rauls

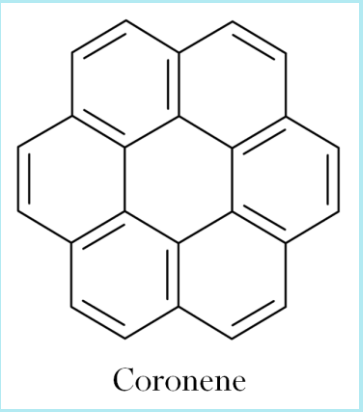




ERC StG “HPAH” (no. 208344)
FP7 Marie Curie Action ITN “LASSIE”

PAHs and H_2 formation

- DFT calculations
  - Efficient superhydrogenation
  - Catalytic formation of H_2 *via* abstraction
- Experimental observations
  - Formation of extensively hydrogenated coronene
  - Indirect evidence for HD (H_2) formation


Coronene

Interstellar PAHs

- Some correlation between H_2 and PAH emission in PDRs with low UV flux
  - Habart *et al.**

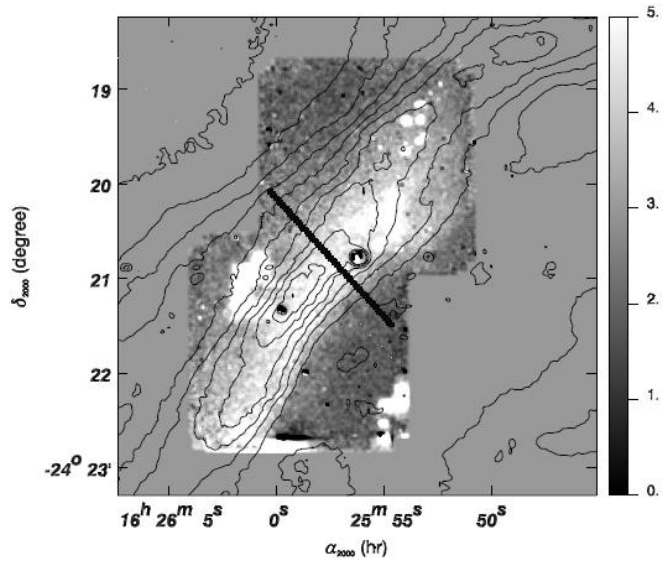


Fig. 2. A map of the bright filament of the western edge of the ρ Ophiuchi main cloud in the 1-0 S(1) H_2 emission line (in 10^{-5} erg s^{-1} cm^{-2} sr^{-1}) obtained at ESO (grey scale). Contours of PAH emission in the LW2 filter are superposed. The brightness profile along the cut marked here is shown in Fig. 5.

*Habart *et al.*, A&A, **397**, 623 (2003)
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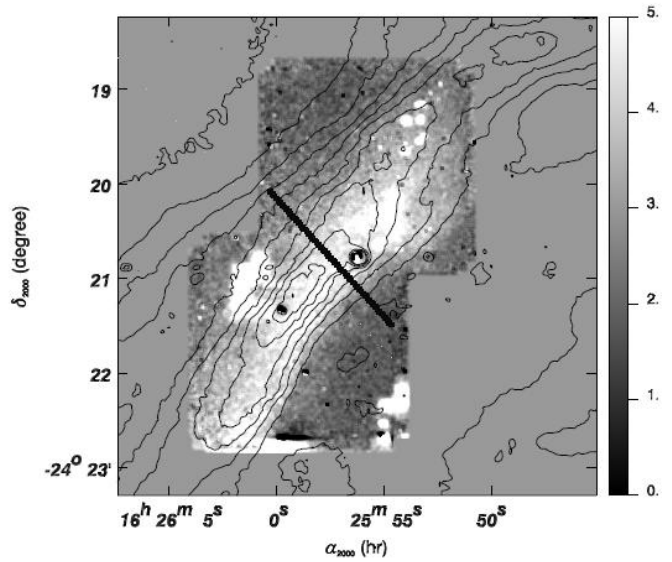
- PAH cations considered for H_2 formation
  - Snow *et al.*^
  - LePage *et al.*#



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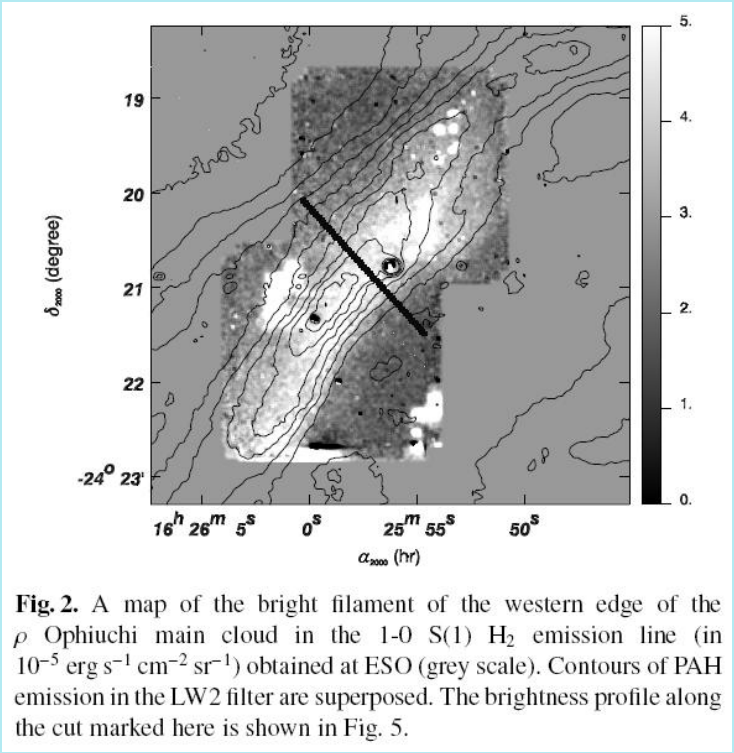
But what about the role of neutral PAHs?



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Interstellar PAHs

- High UV flux
  - Small PAHs dissociated
- Intermediate UV flux
  - Dehydrogenation
  - Ionization
- Low UV flux
  - Higher hydrogenation states for large PAHs stable

$$\mathrm{PAH} + h\nu \rightarrow \mathrm{Products}$$

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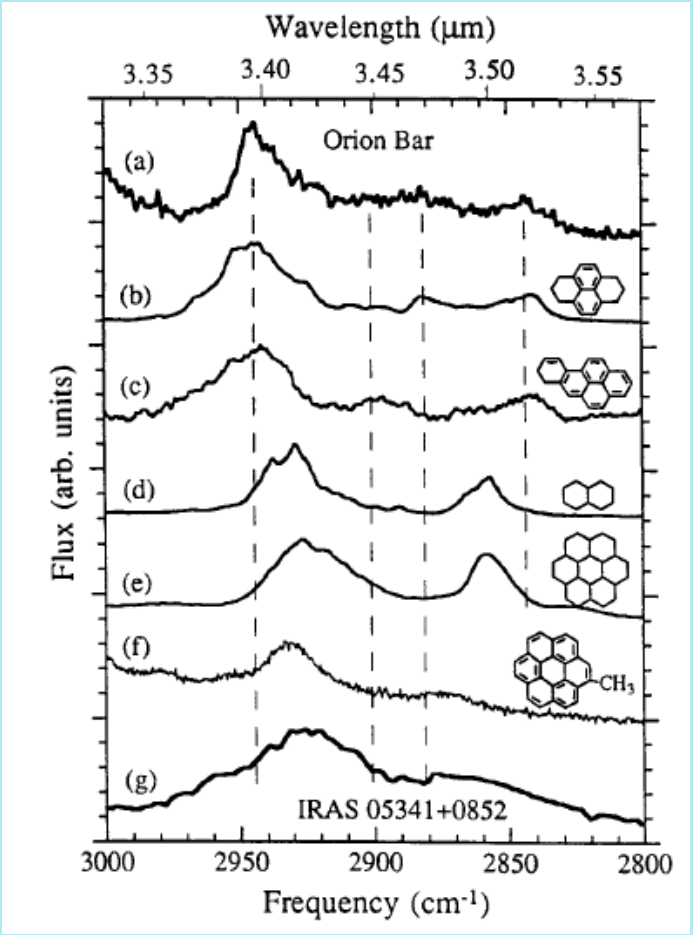
$$\mathrm{PAH} + h\nu \rightarrow \mathrm{PAH}^{+} + e^{-}$$

$$\mathrm{PAH} + \mathrm{H} \rightarrow \mathrm{HPAH}$$

V. Le Page, *et al.*, ApJSS, **132**, 233 (2001)/ ApJ, **584**, 316 (2003)

Superhydrogenated PAHs

- Evidence in IR emission
  - C-H stretching mode
    - 3.3 μm – aromatic
    - 3.4 μm – aliphatic
- High UV flux (Orion bar)
  - Limited excess hydrogen
- Low UV flux (IRAS 05341)
  - Significant excess hydrogen
  - $-CH_3$ or -H



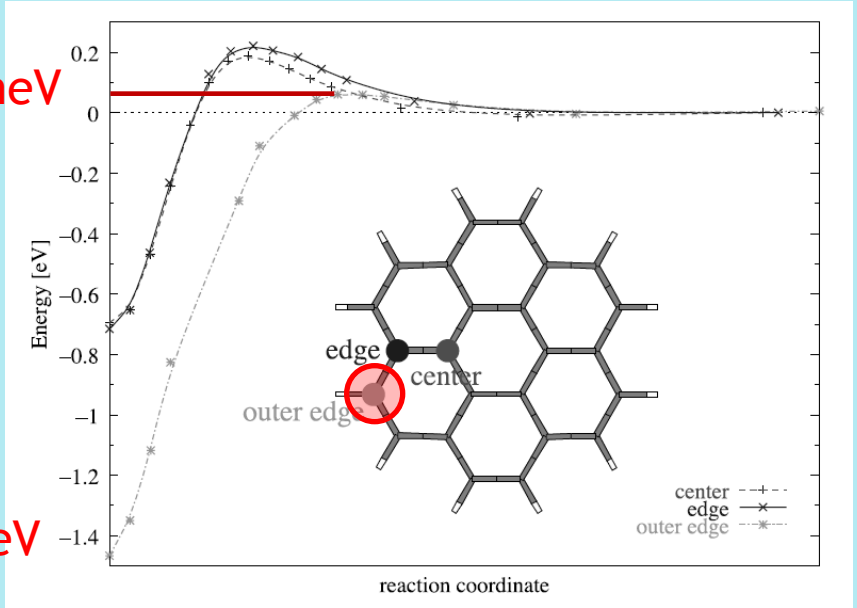
M. P. Bernstein, *et al.*, ApJ, **472**, L127 (1996).

Hydrogenation of Coronene

- DFT Calculations
  - Addition of 1st H
  - Outer edge site
    - Small barrier
      - Graphite -> 200 meV
    - Strongly bound
      - Graphite -> 700 meV
  - Lower gas temperatures viable

60 meV

-1.4 eV

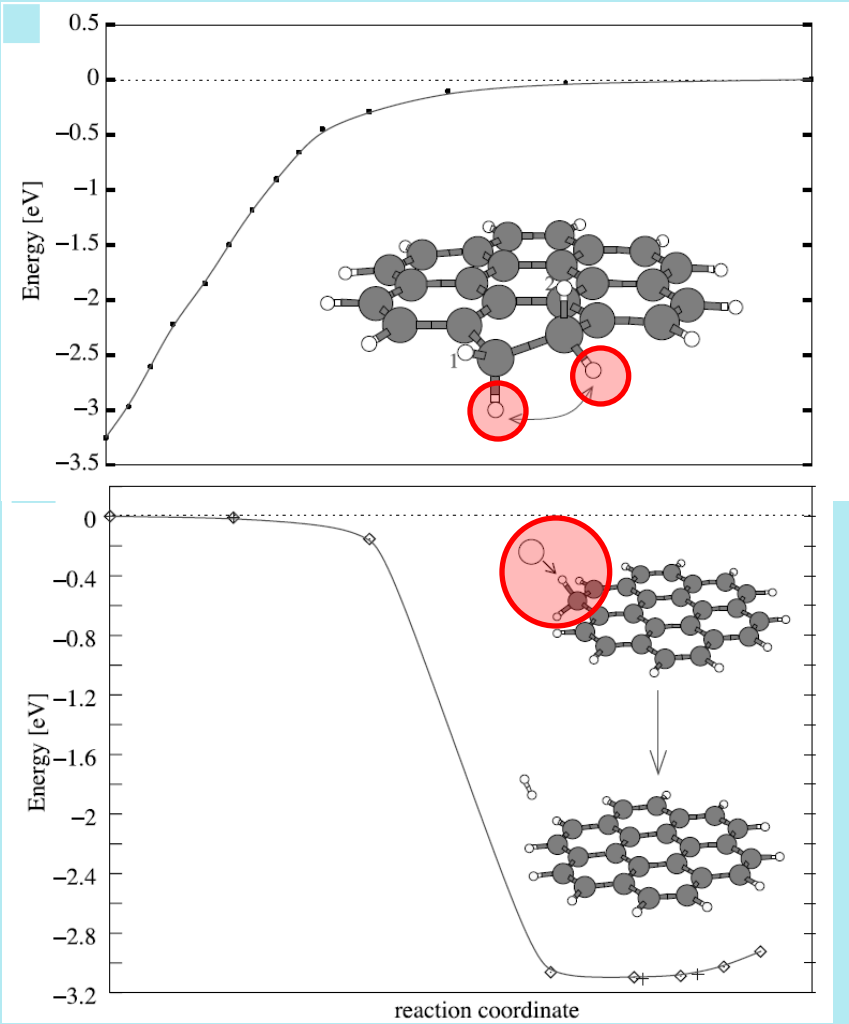


$C_{24}H_{13}$ ← $C_{24}H_{12}$ + H

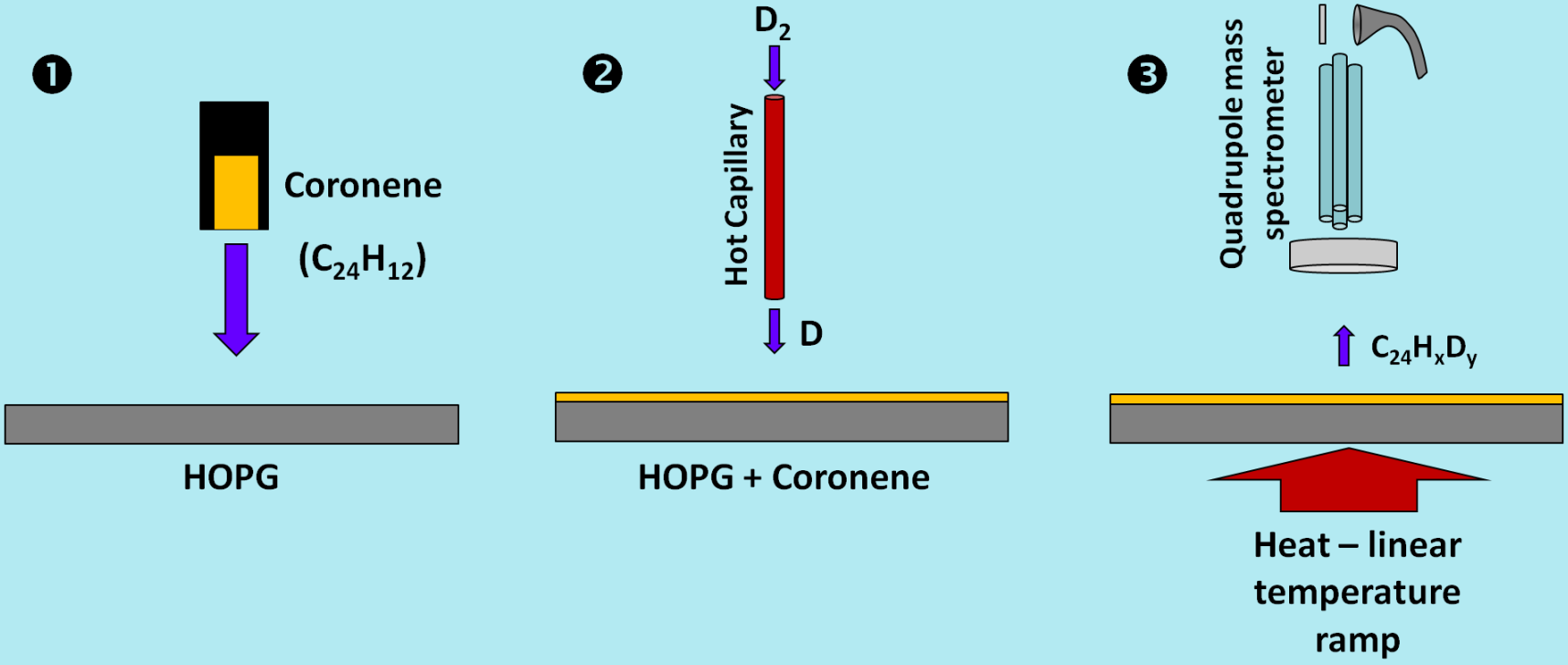
E. Rauls & L. Hornekær, *Astrophys. J.*, **679**, 531 (2008).

H_2 formation *via* abstraction

- DFT Calculations
  - Barrierless addition of 2nd H
    - Large binding energy
  - Barrierless H abstraction by 2nd H
    - H_2 formation
  - Competition between absraction and addition (low/vanishing barriers)
  - Higher degrees of hydrogenation, including center sites, also favourable

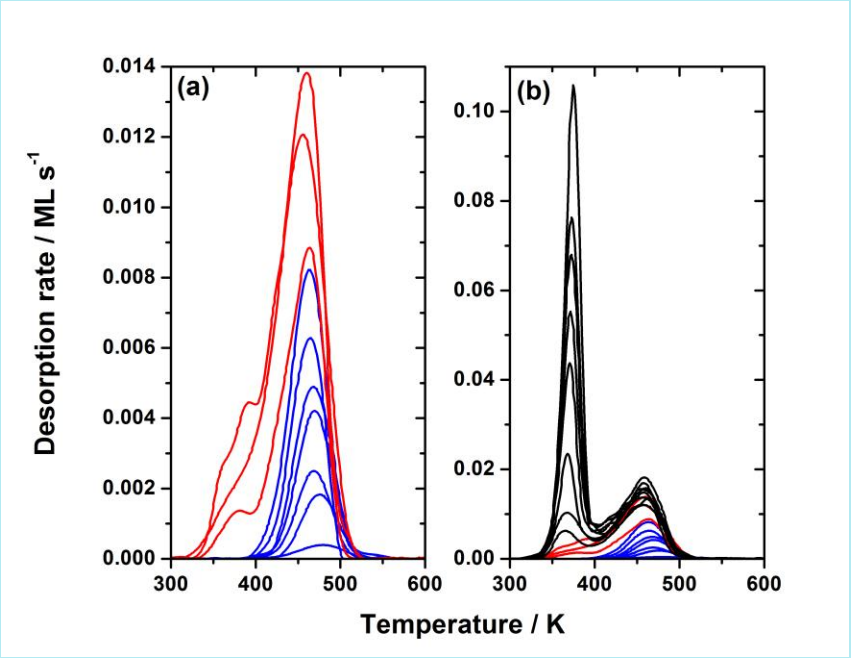


Experimental arrangement



TPD: $C_{24}H_{12}$ from graphite

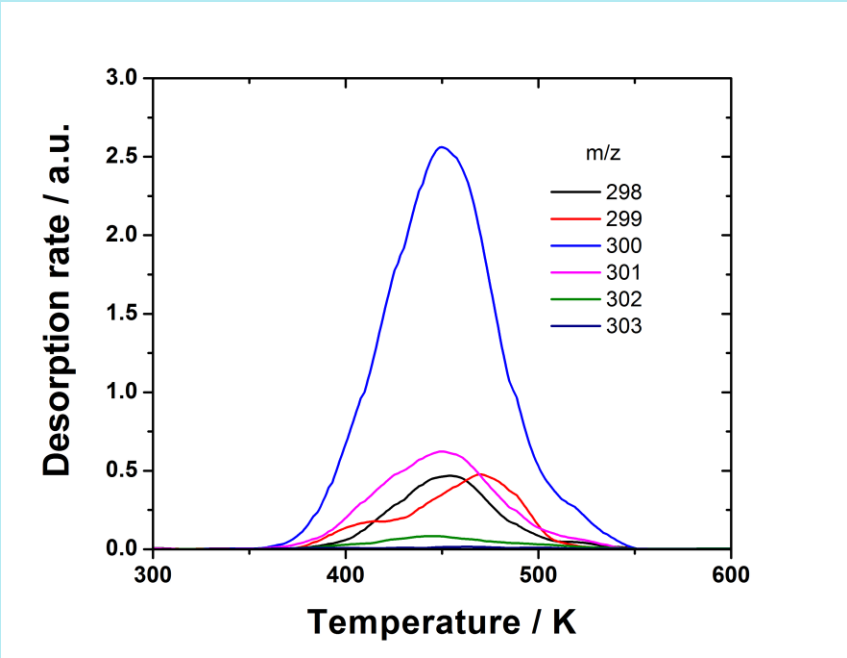
- Graphite (HOPG) exposed to $C_{24}H_{12}$
- Thermal desorption @ 1 K/s
  - Monitor *m*/*z*=300 (parent ion)
- Resolve mono- and multilayers
- Multilayers consistent with previous study†
  - Desorption energy *ca*. 1.5 eV



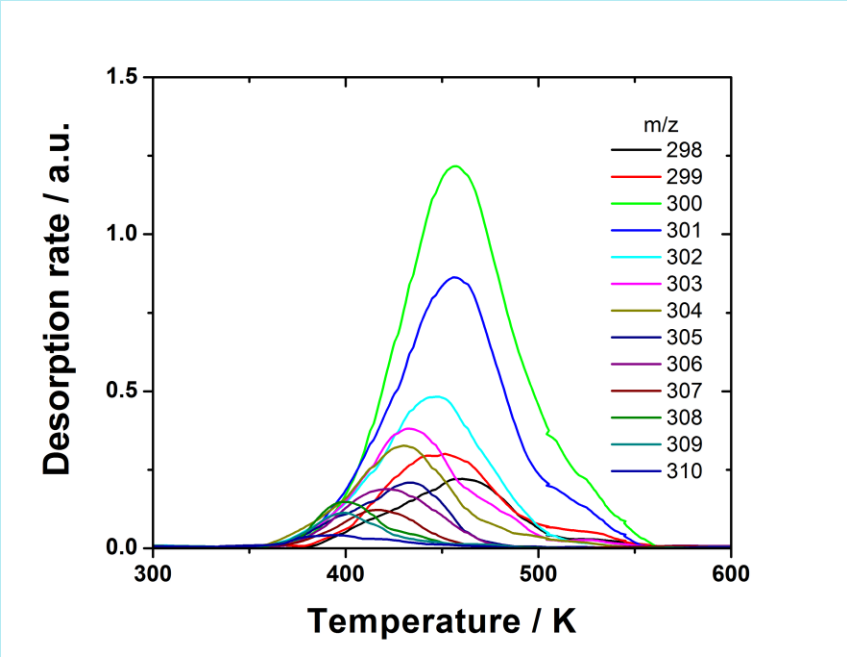
† R. Zacharia, *et al.*, *Phys. Rev. B*, **69**, 155406 (2004).

Hydrogenation of Coronene

Coronene TPD



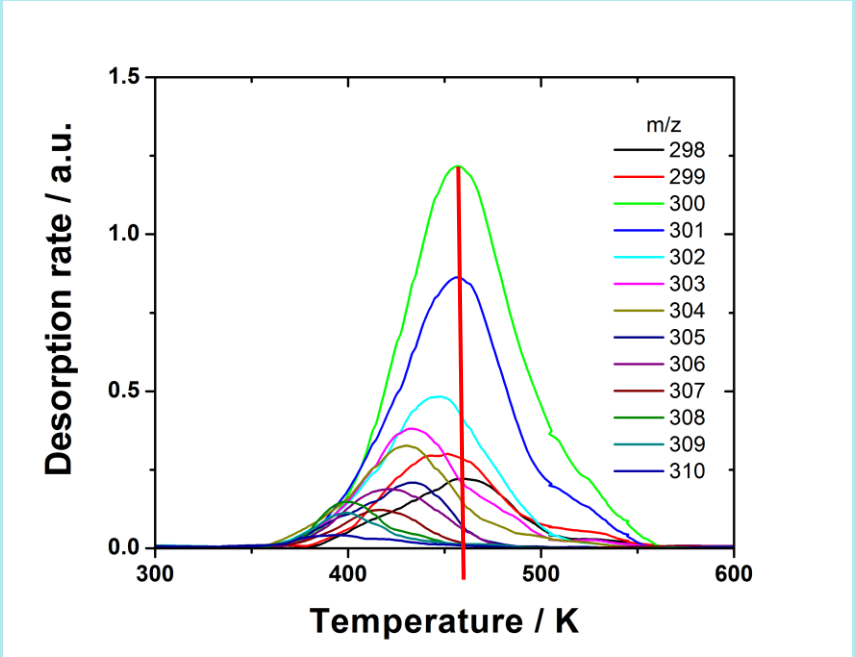
Coronene exposed to 5 min D
$\varphi=10^{16}$ D atoms cm^{-2}



Evidence for hydrogenation of coronene through detection of $C_{24}H_xD_y$

Hydrogenation of Coronene

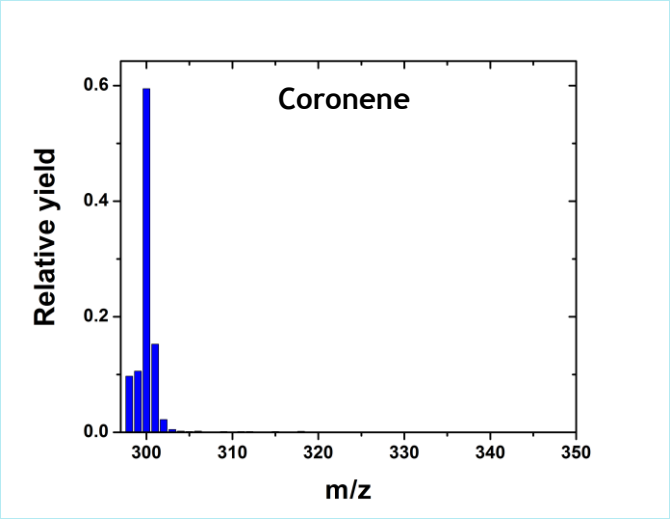
- Hydrogenated coronene desorbs at slightly lower temperature
- Cf. C_6H_{12} desorbing at lower temperature than C_6H_6[†]



[†] M. Xi, *et al.*, J. Vac. Sci. Technol. B, **10**, 2440 (1992).

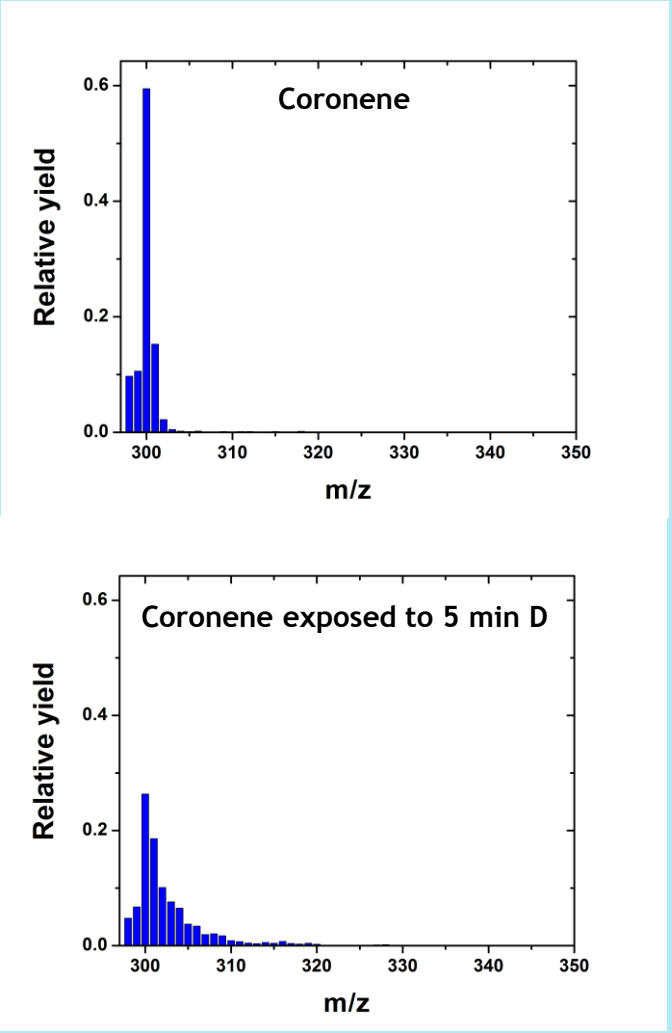
Hydrogenation of Coronene

- Mass spectra of desorbed species
  - Integrated over TPD peak
  - Expected fragmentation / isotope peaks for coronene



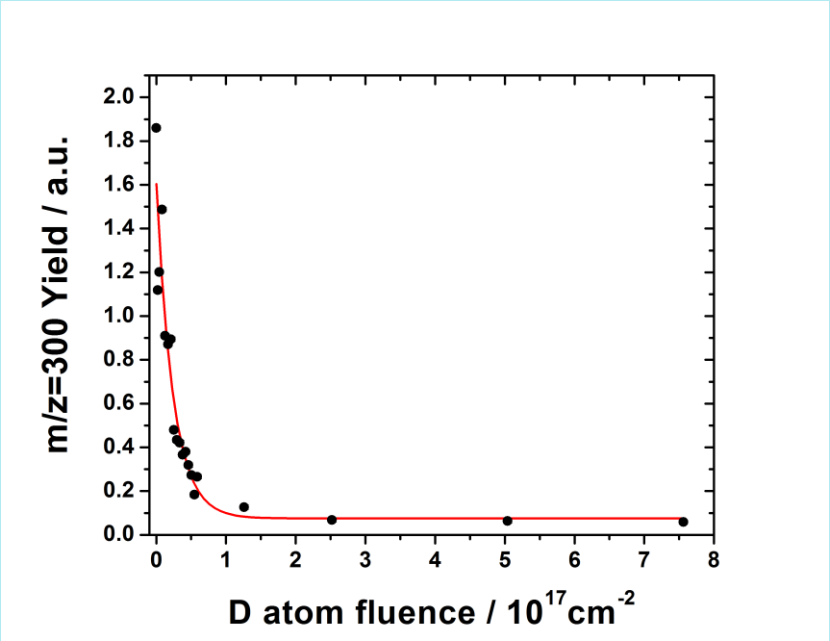
Hydrogenation of Coronene

- Mass spectra of desorbed species
  - Integrated over TPD peak
  - Expected fragmentation / isotope peaks for coronene
- Exposure to atomic D
  - Clear evidence for superhydrogenated species
  - Simultaneous loss of parent coronene



Decay of Coronene Yield

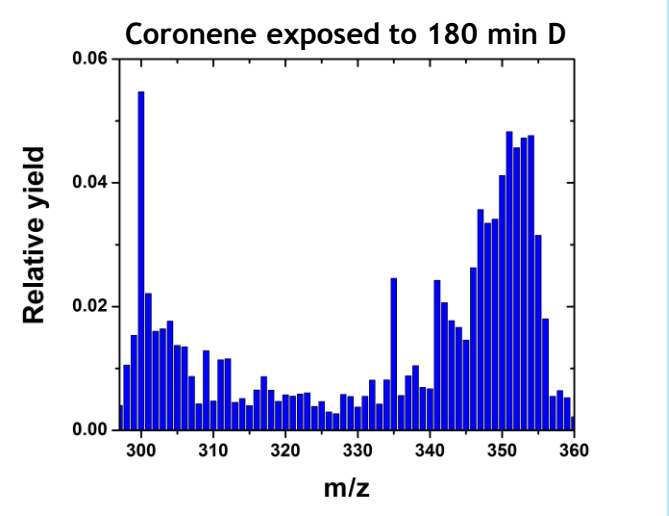
- Significant loss of coronene
  - Single layer
  - Efficient hydrogenation
  - σ=0.4 Å^2

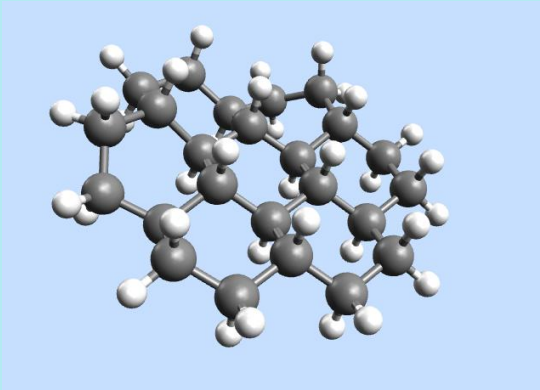


$$C_{m300} = A\exp(-\sigma\varphi)$$

Hydrogenation of Coronene

- Long exposure times
  - Extensive hydrogenation
  - Dominated by high *m/z*
  - Close to limiting case (m/z=360)

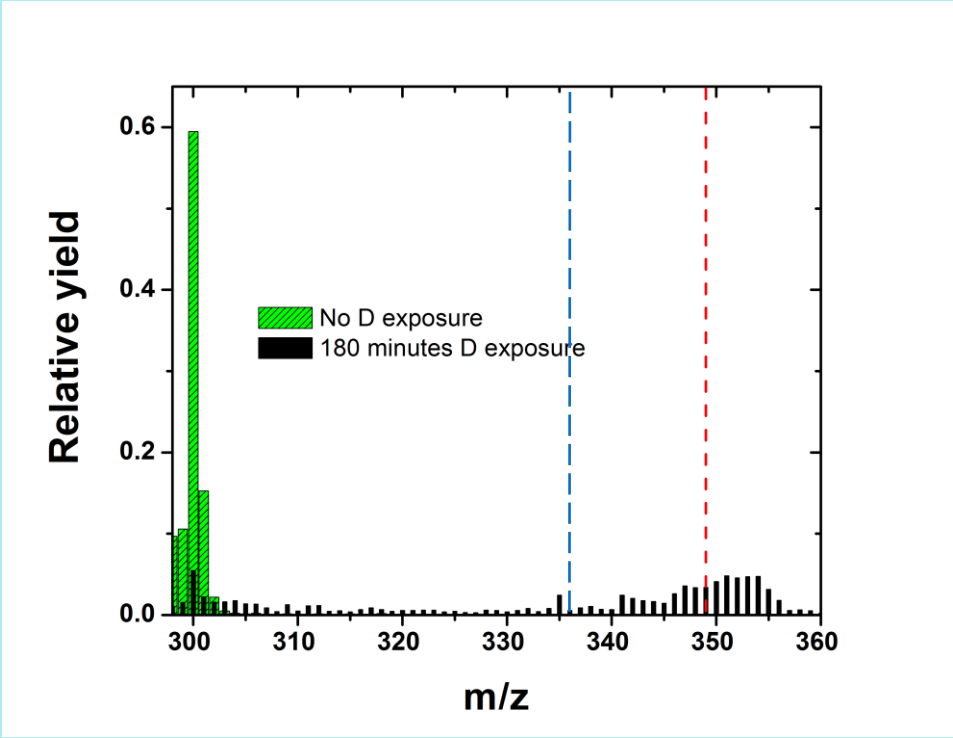




Perhydrocoronene

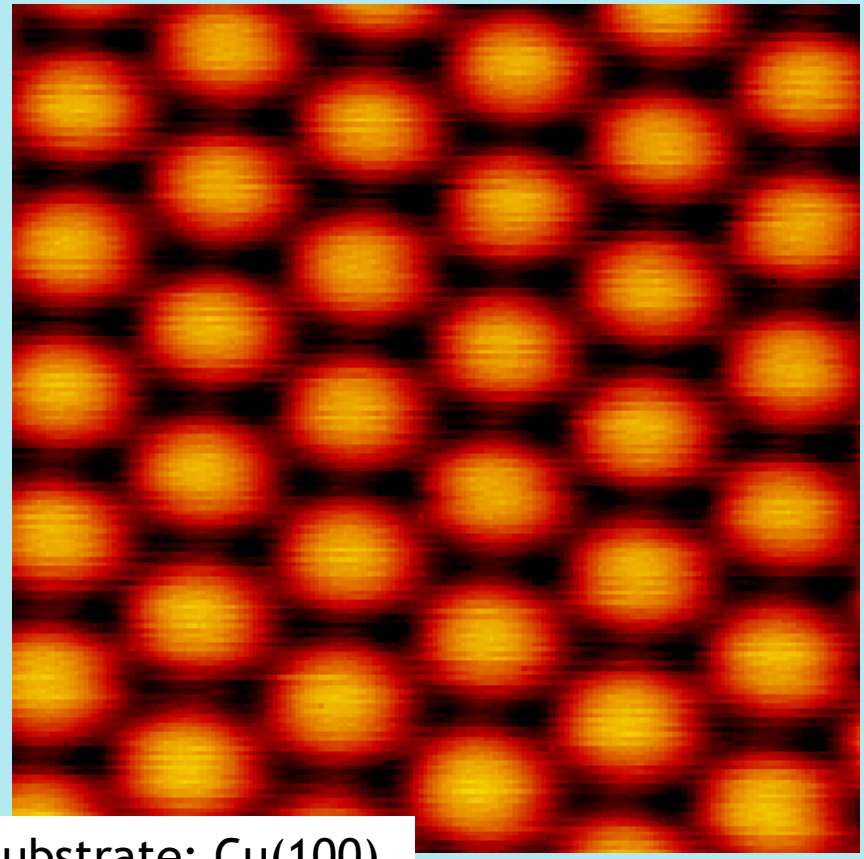
Hydrogenation of Coronene

- Long exposure times
  - Close to limiting case (m/z=360)
- Above m/z=336 confirms **hydrogenation of center sites**



Hydrogenation: STM images

Coronene

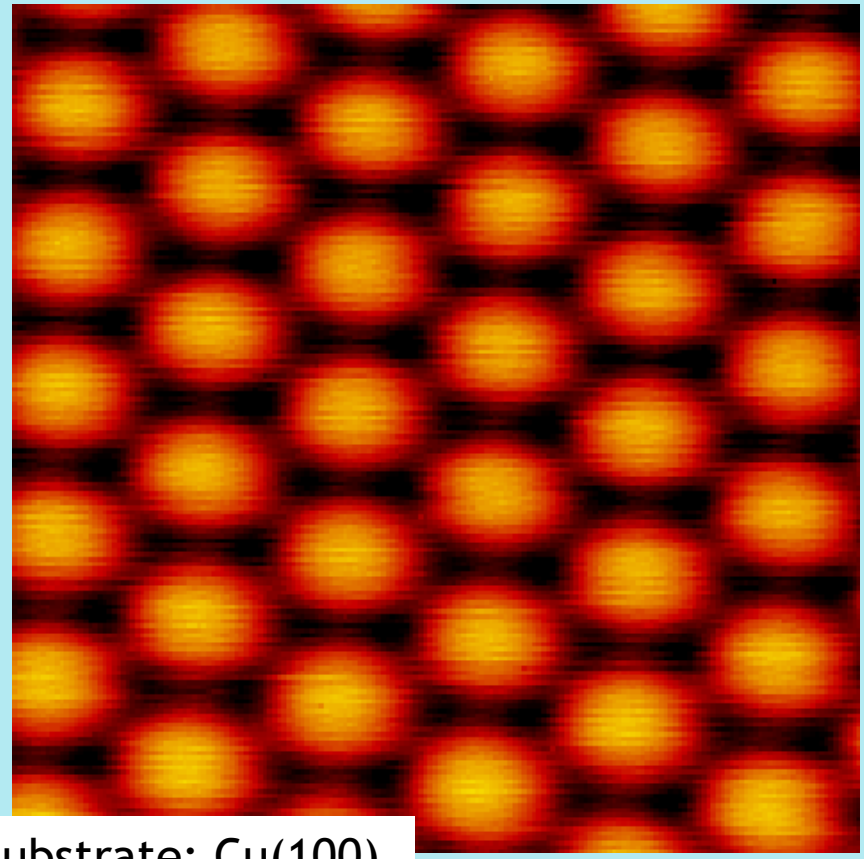


Substrate: Cu(100)

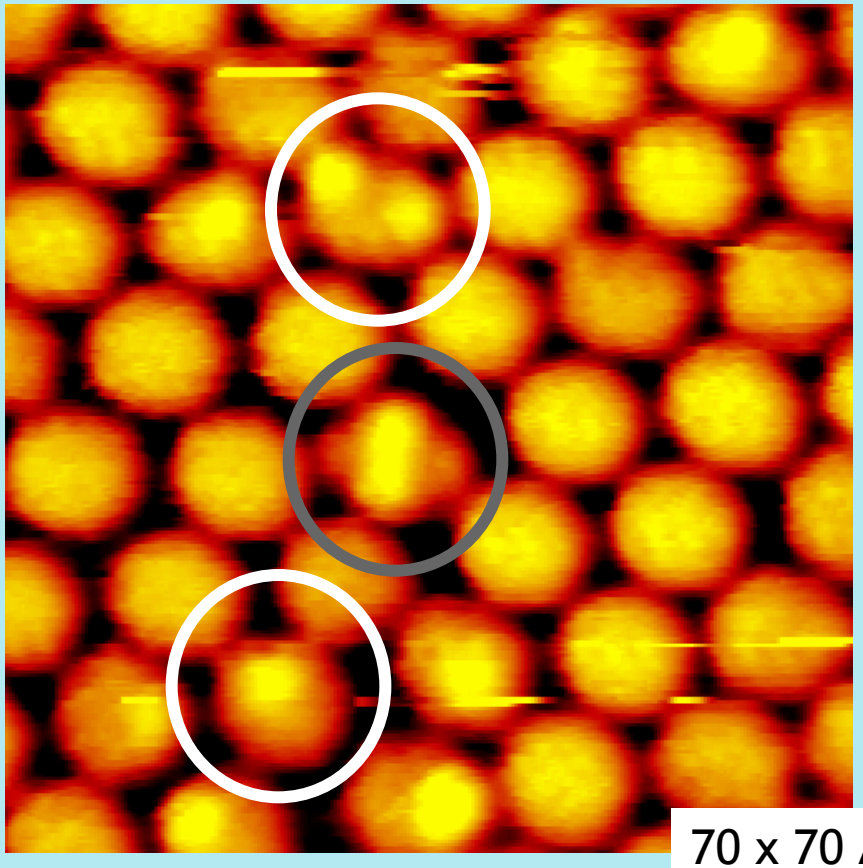
70 x 70 Å

Hydrogenation: STM images

Coronene



Coronene exposed to D



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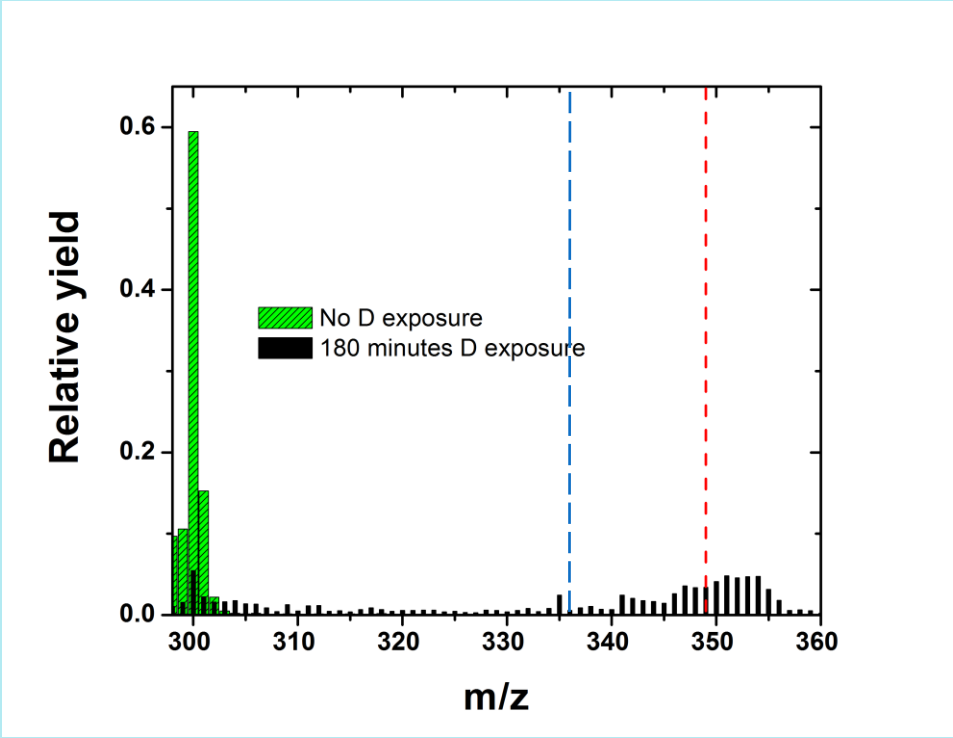
Hydrogenation of Coronene

- Long exposure times
  - Close to limiting case (m/z=360)
- Above m/z=336 confirms **hydrogenation of center sites**
- Above m/z=348 requires H-D exchange
  - Implies abstraction reactions
  - **=> HD (H_2 formation)**



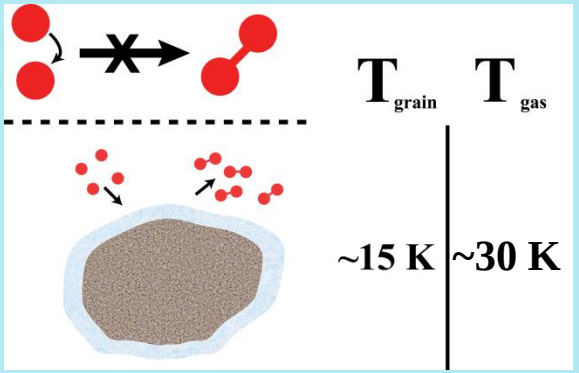
Thank you for your attention

Interstellar H_2 formation

- The “well-known” problem

Interstellar H_2 formation

- The “well-known” problem
- Surface reactions
  - Low T
    - Physisorption on ice surfaces



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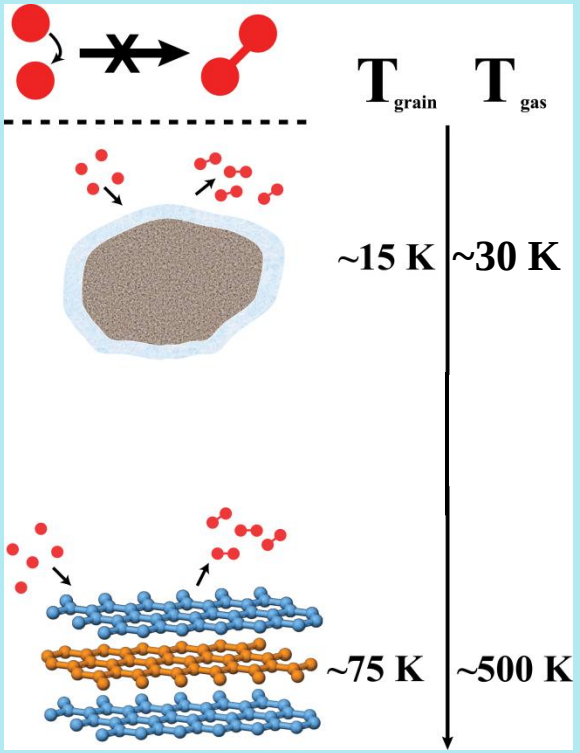
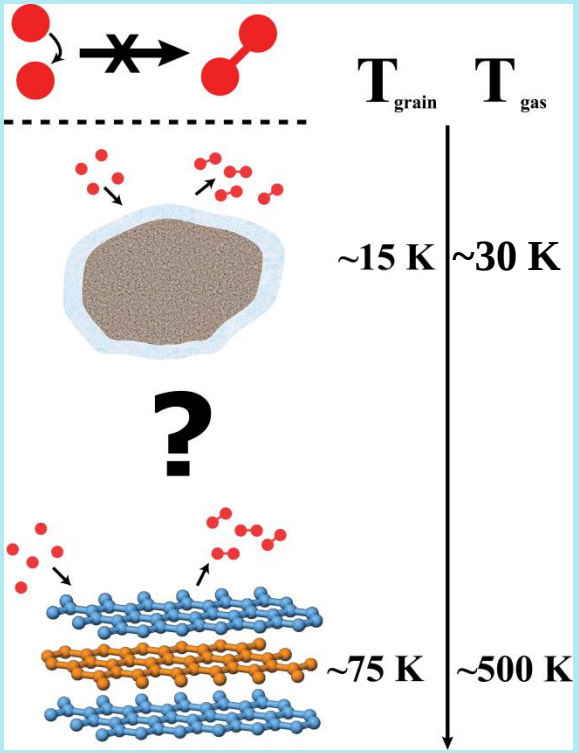
  - High T
    - Chemisorption on carbonaceous surfaces



Interstellar H_2 formation

- The “well-known” problem
- Surface reactions
  - Low T
    - Physisorption on ice surfaces
  - High T
    - Chemisorption on carbonaceous surfaces
  - Intermediate T
    - PAHS?



Conclusions

- DFT calculations and experimental observations:

- Show efficient superhydrogenation (including center sites) of coronene
- Indirect evidence for HD (H_2) formation through abstraction reactions

Conclusions

- DFT calculations indicate efficient superhydrogenation of coronene
- Experimental observation of superhydrogenated coronene
  - Clear evidence for extensive hydrogenation
  - Indirect evidence for HD (H_2) formation through abstraction reactions

3.12 **3.31** **3.64**

See posters by Andrew Cassidy, Emil Friis and Vito Mennella

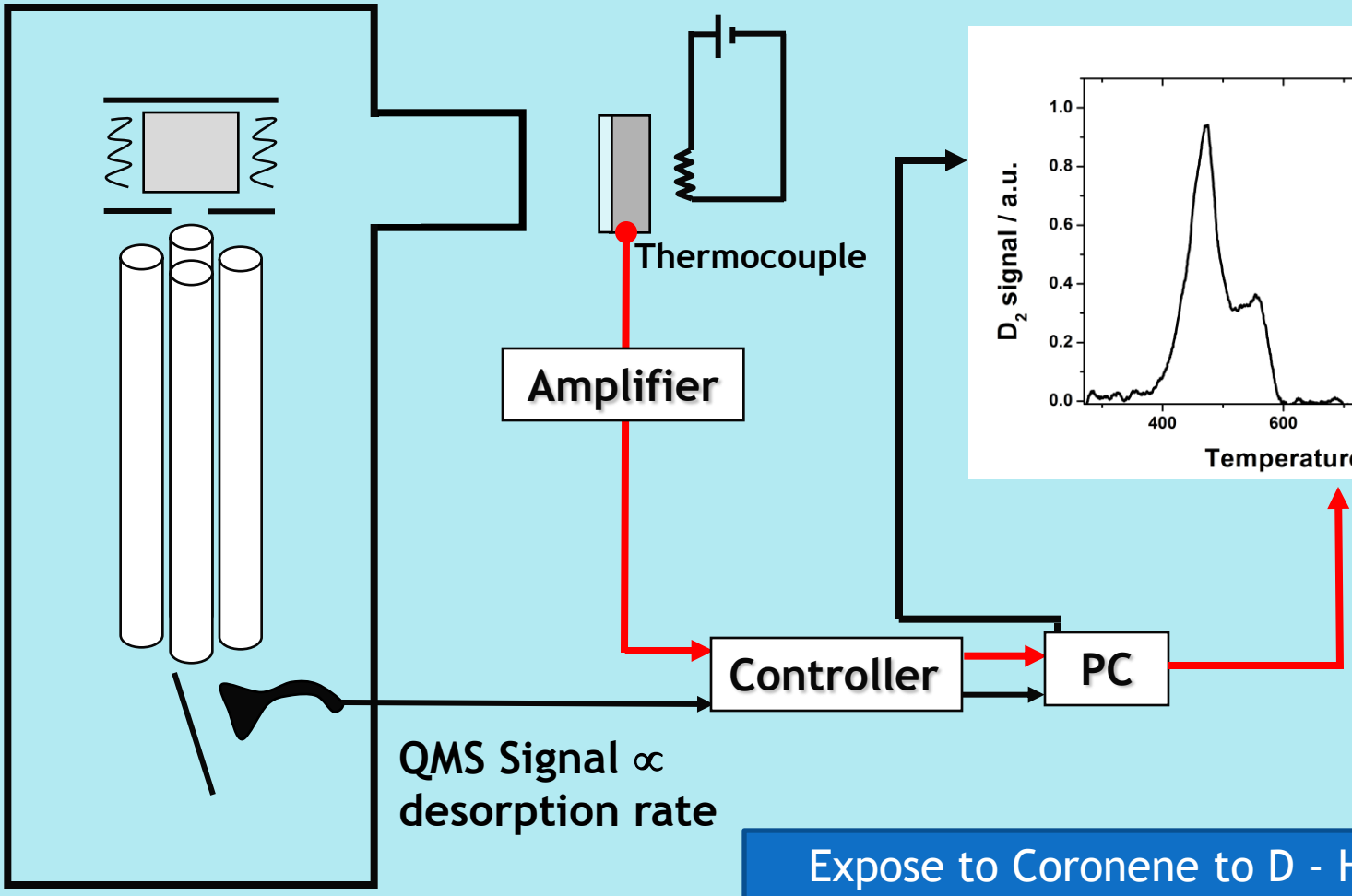
STM **TPD** **IR**

STM parameters (Cu)

- Coronene
  - V_t=-3500 mV
  - I_t=-0.1 nA

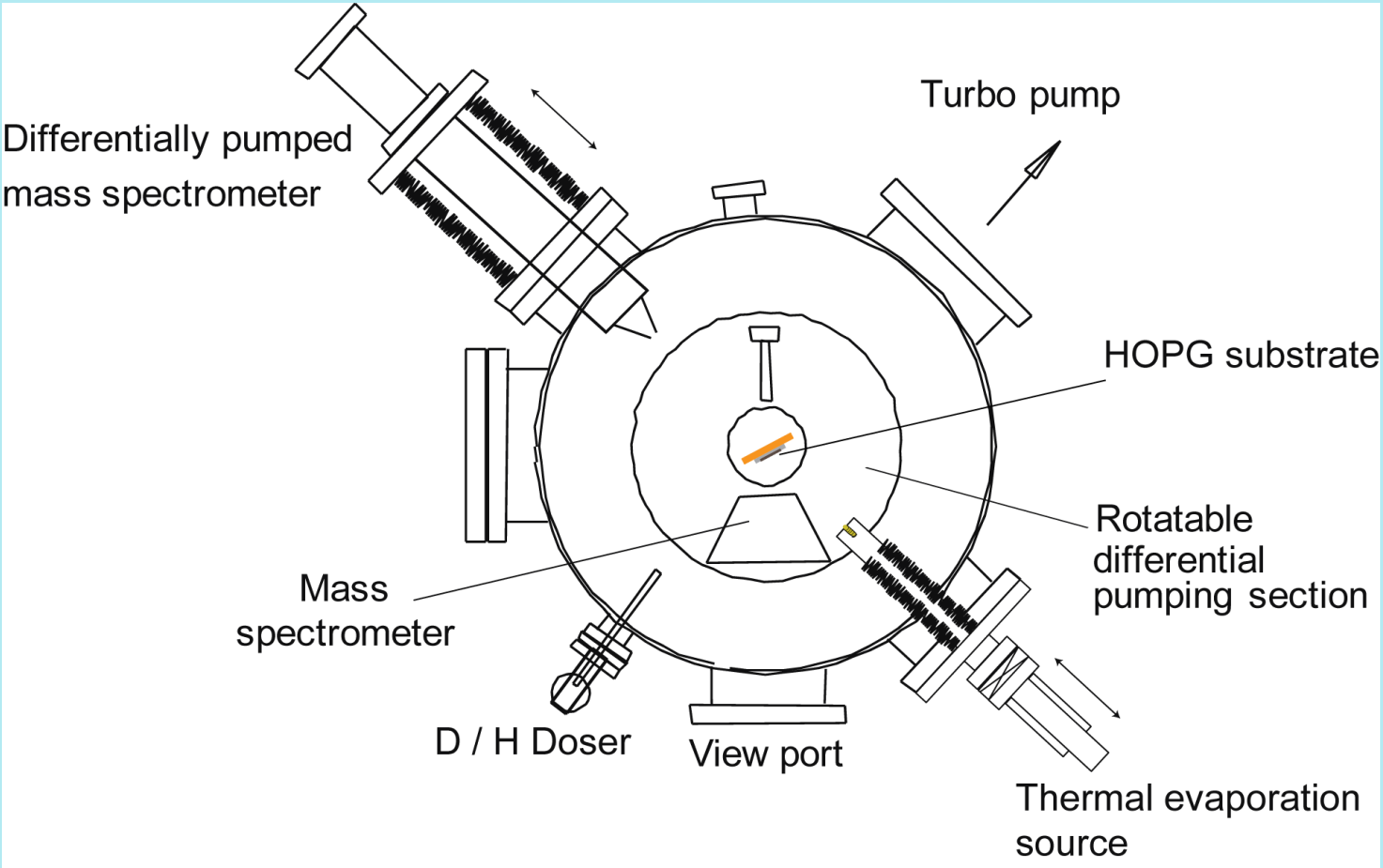
- Coronene exposed to D
  - V_t=-1900 mV
  - I_t=-0.2 nA

Thermal desorption (TPD)



Expose to Coronene to D - Hot (~2100 K)

Experimental arrangement



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- Intermediate UV flux
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  - Ionization

Low UV flux

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$$\mathrm{PAH} + h\nu \rightarrow \mathrm{PAH}^{+} + e^{-}$$

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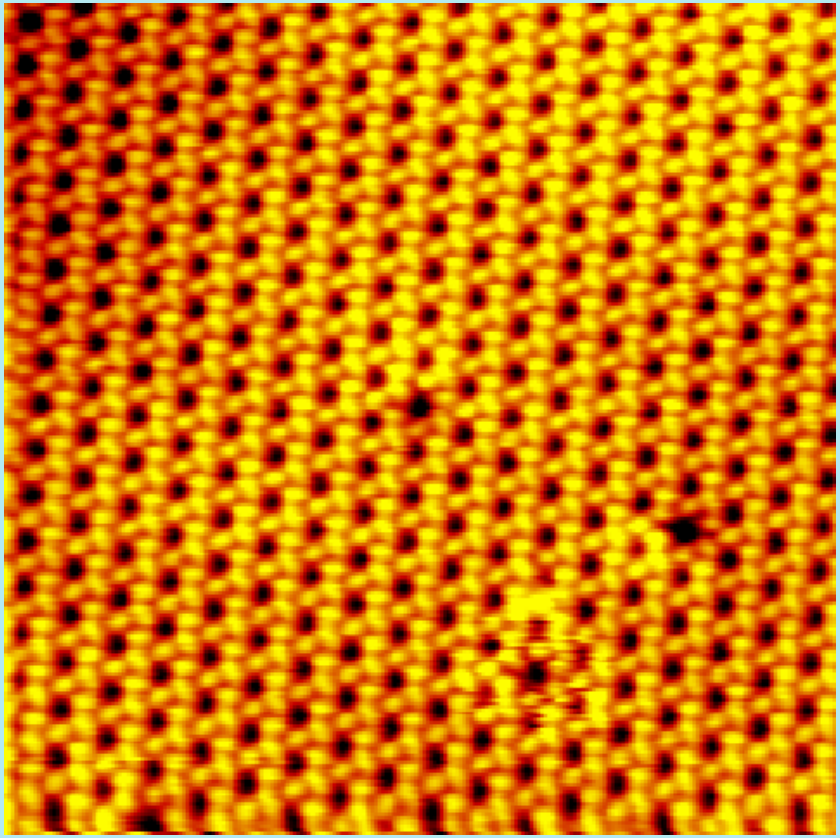
V. Le Page, *et al.*, ApJSS, **132**, 233 (2001).

Hydrogenation: STM images

Coronene

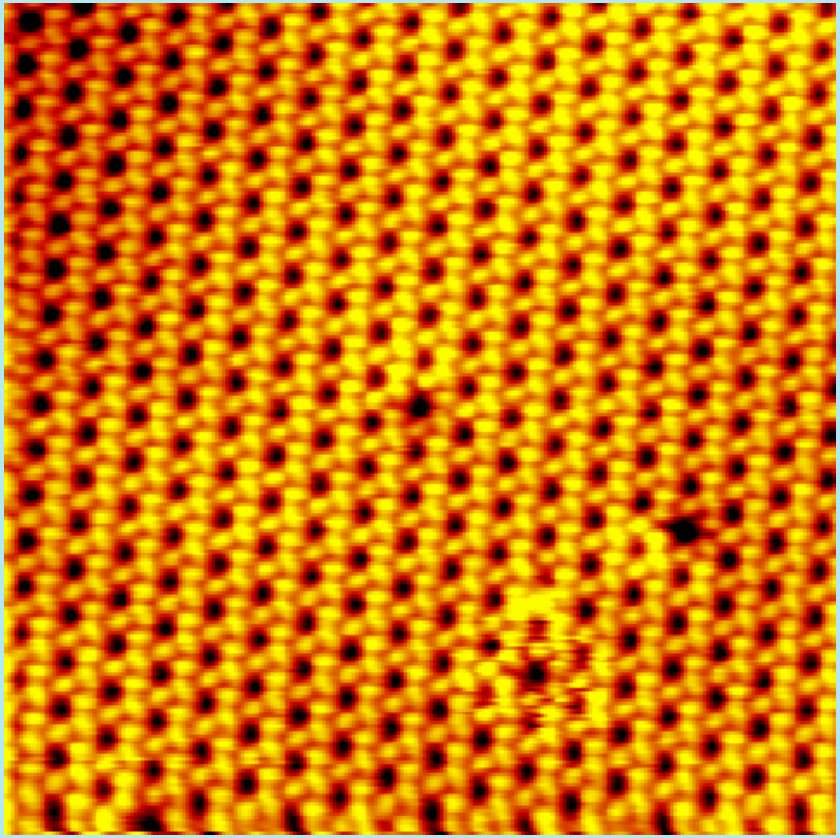


Substrate: HOPG

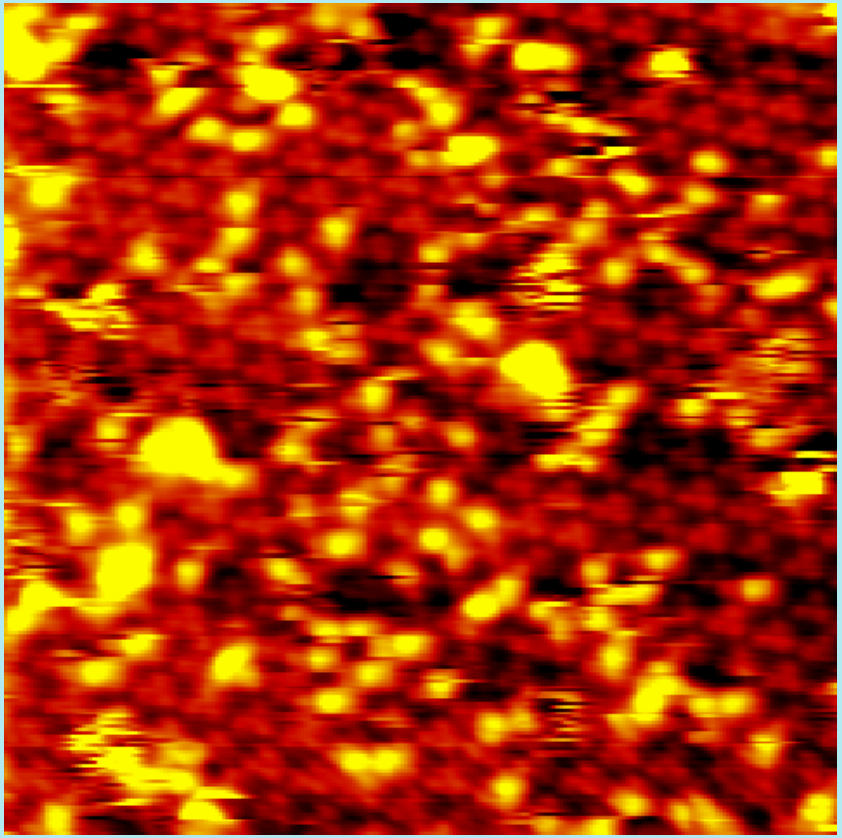
200 x 200 Å

Hydrogenation: STM images

Coronene



Coronene exposed to D



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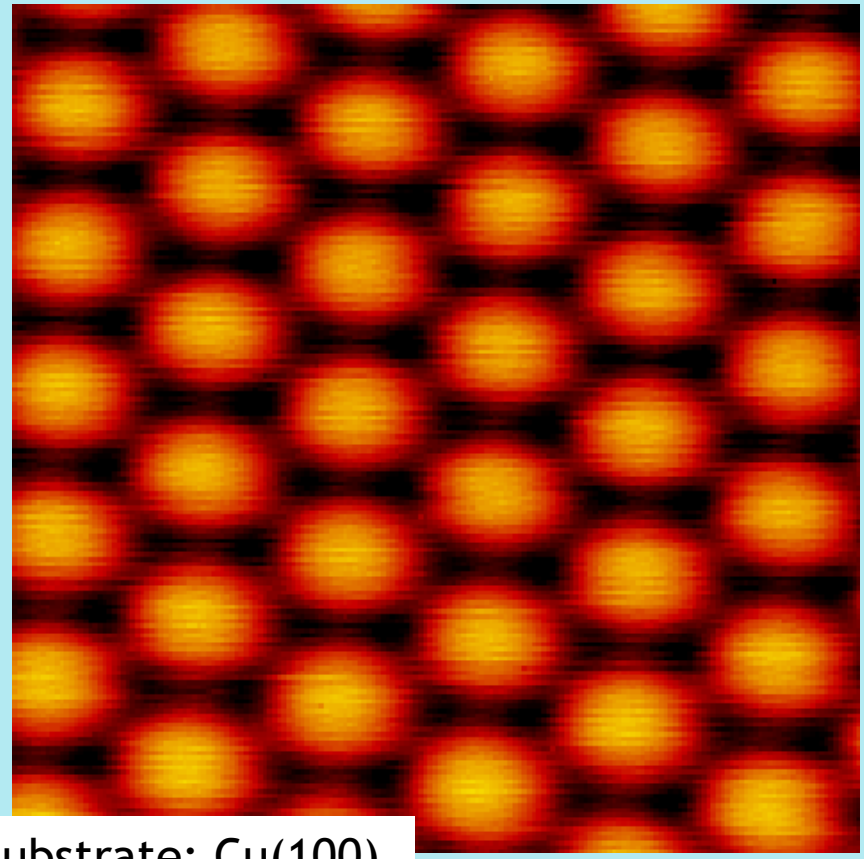

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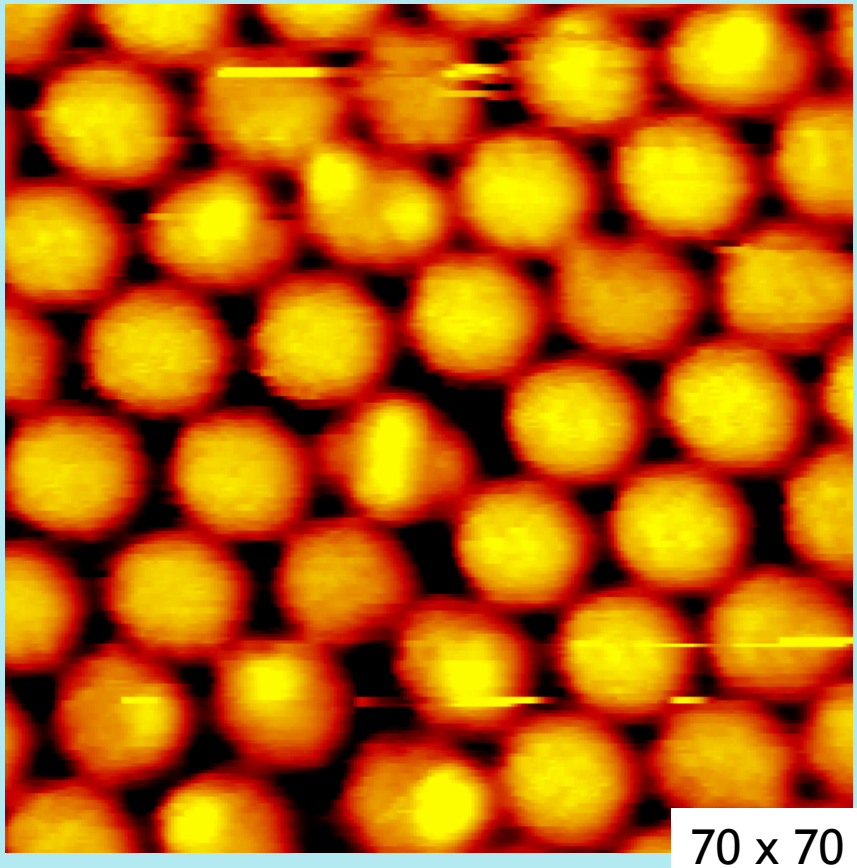

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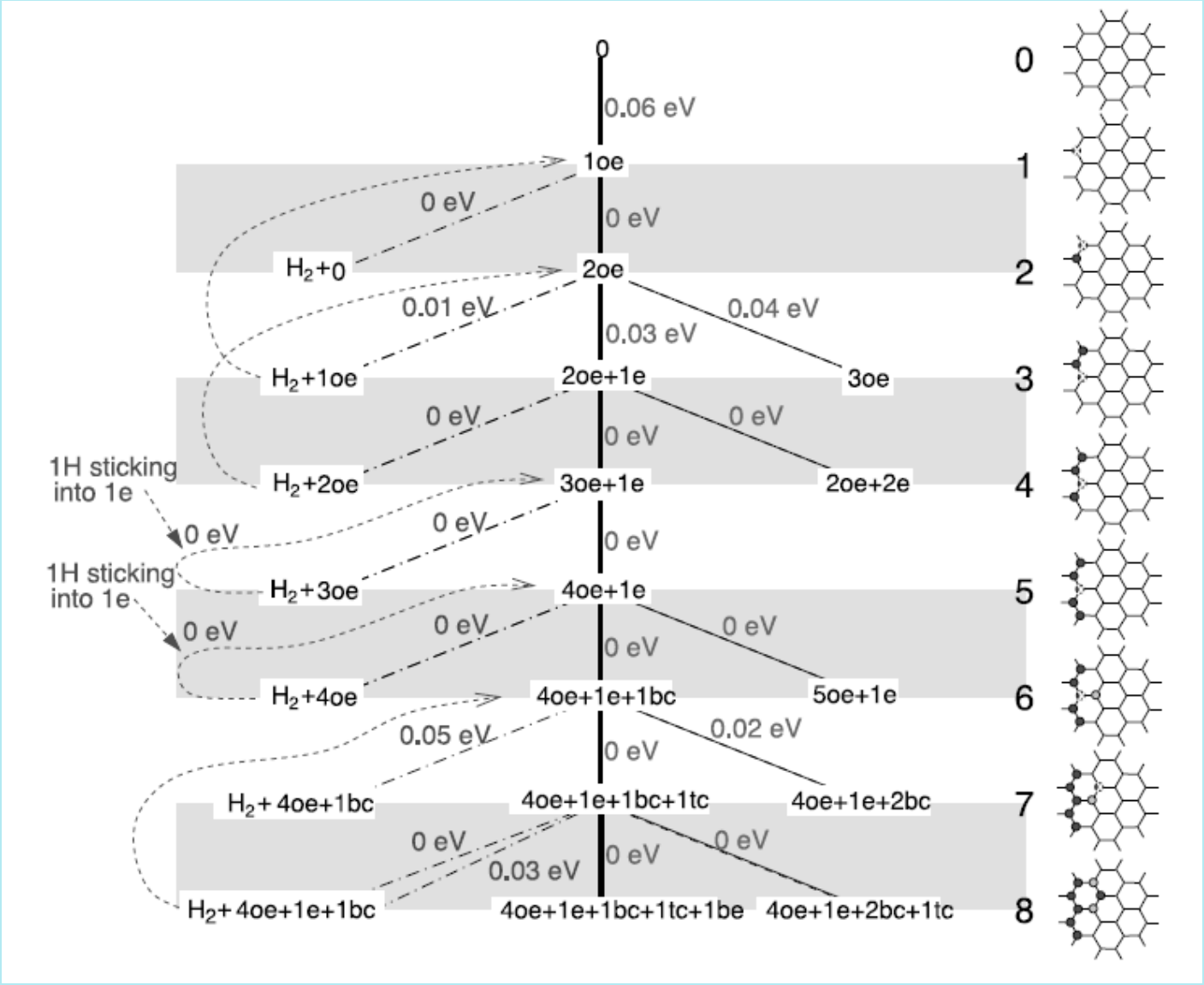
0
0.06 eV
1oe
0 eV
0 eV
H2+0
2oe
0.01 eV
0.04 eV
0.03 eV
H2+1oe
2oe+1e
3oe
0 eV
0 eV
0 eV
H2+2oe
3oe+1e
2oe+2e
1H sticking into 1e
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0 eV
1H sticking into 1e
H2+3oe
4oe+1e
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4oe+1e+1bc
5oe+1e
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4oe+1e+1bc+1tc+1be
4oe+1e+2bc+1tc
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