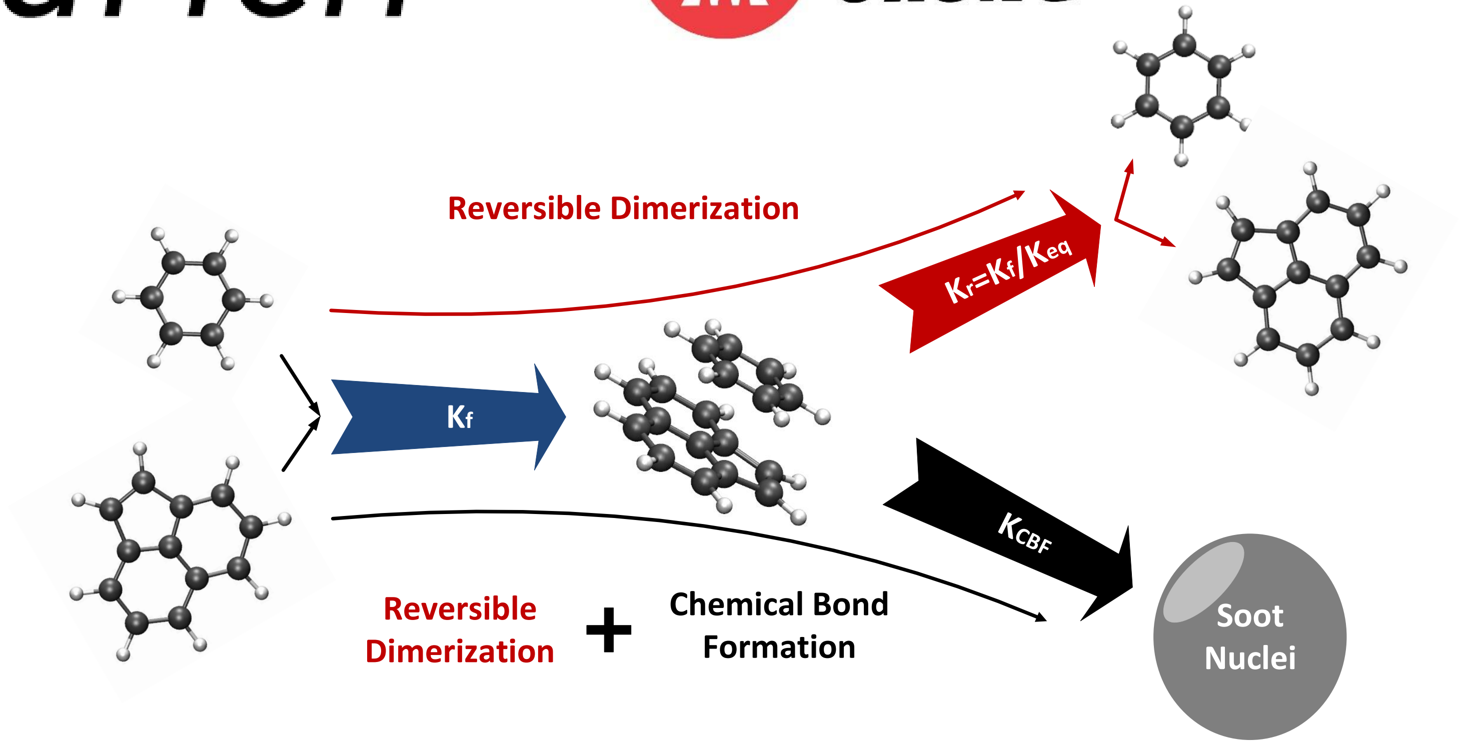
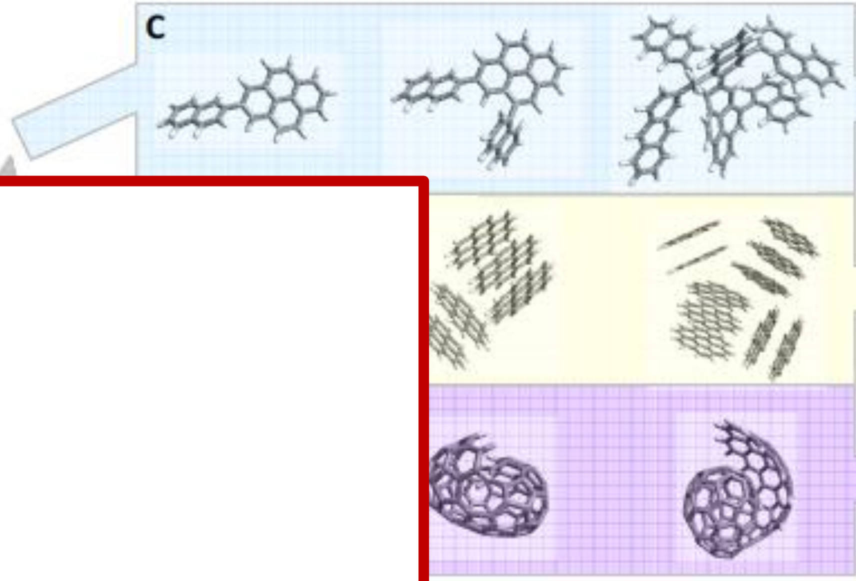


Reactive Polycyclic Aromatic Hydrocarbon Dimerization Drives Soot Nucleation

M. Reza Kholghy, G. A. Kelesidis, S. E. Pratsinis
Particle Technology Laboratory, ETH Zürich, Switzerland

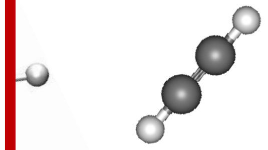
The Nucleation Mystery

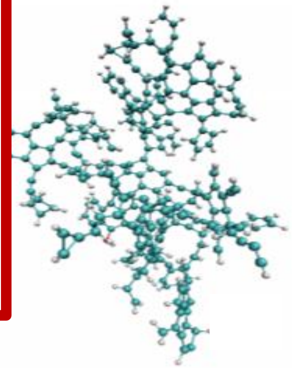


- How is
- Which
- Is the

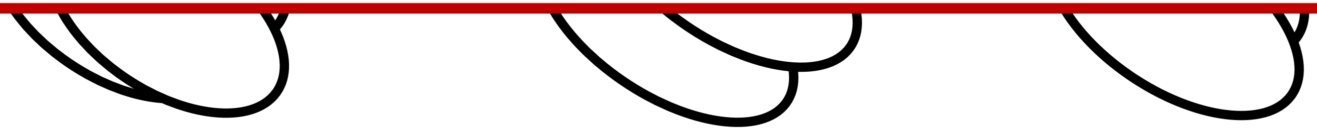
Goal:

a quantitative kinetic model
for
soot nucleation





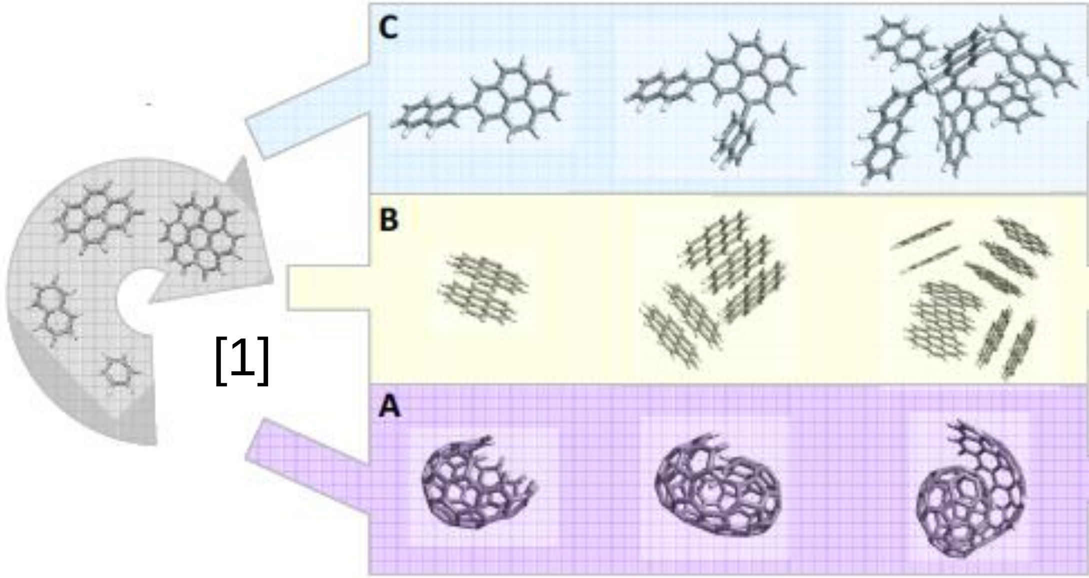
[2]



[1] Wang H, *P Combust Inst*, (2011), **33**, 41 .

[2] Violi A, *Combust Flame*, (2004), **139**, 279 .

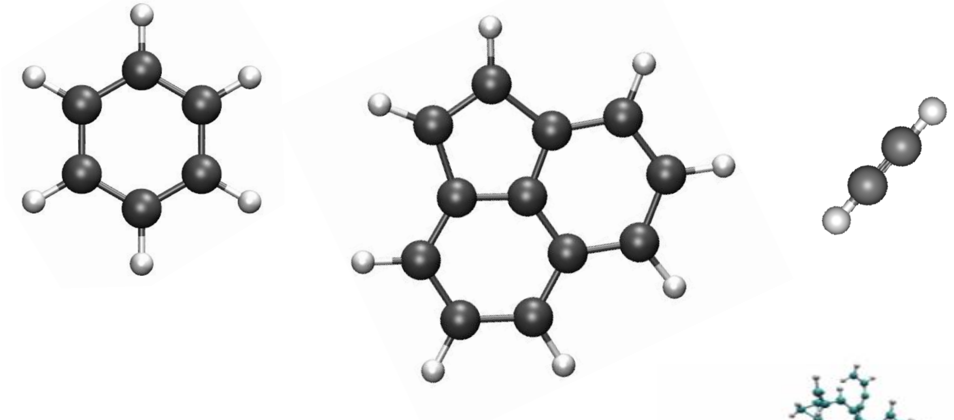
The Nucleation Mystery



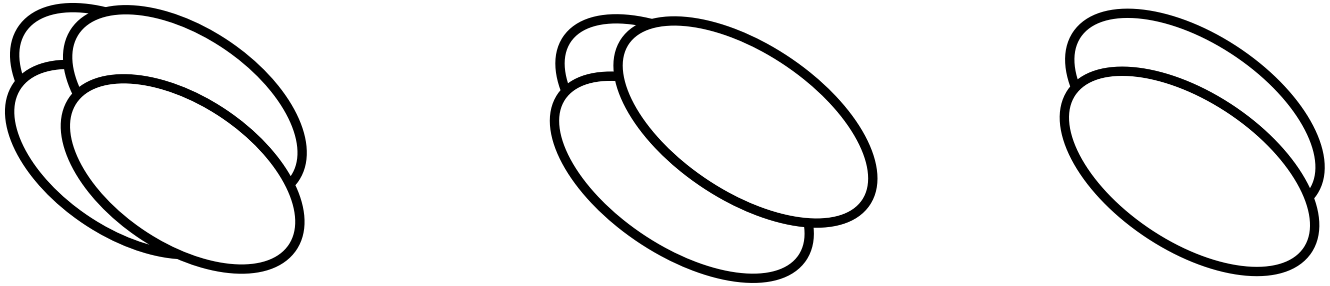
[1]

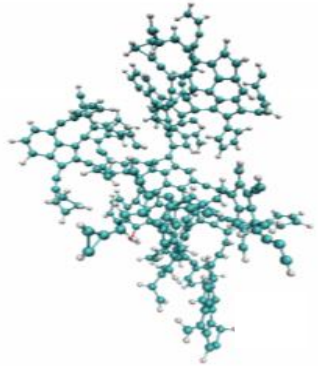
- How is the first soot particle formed?

- Which species form the first soot particle?



- Is the first soot particle a monomer, dimer, trimer or larger?

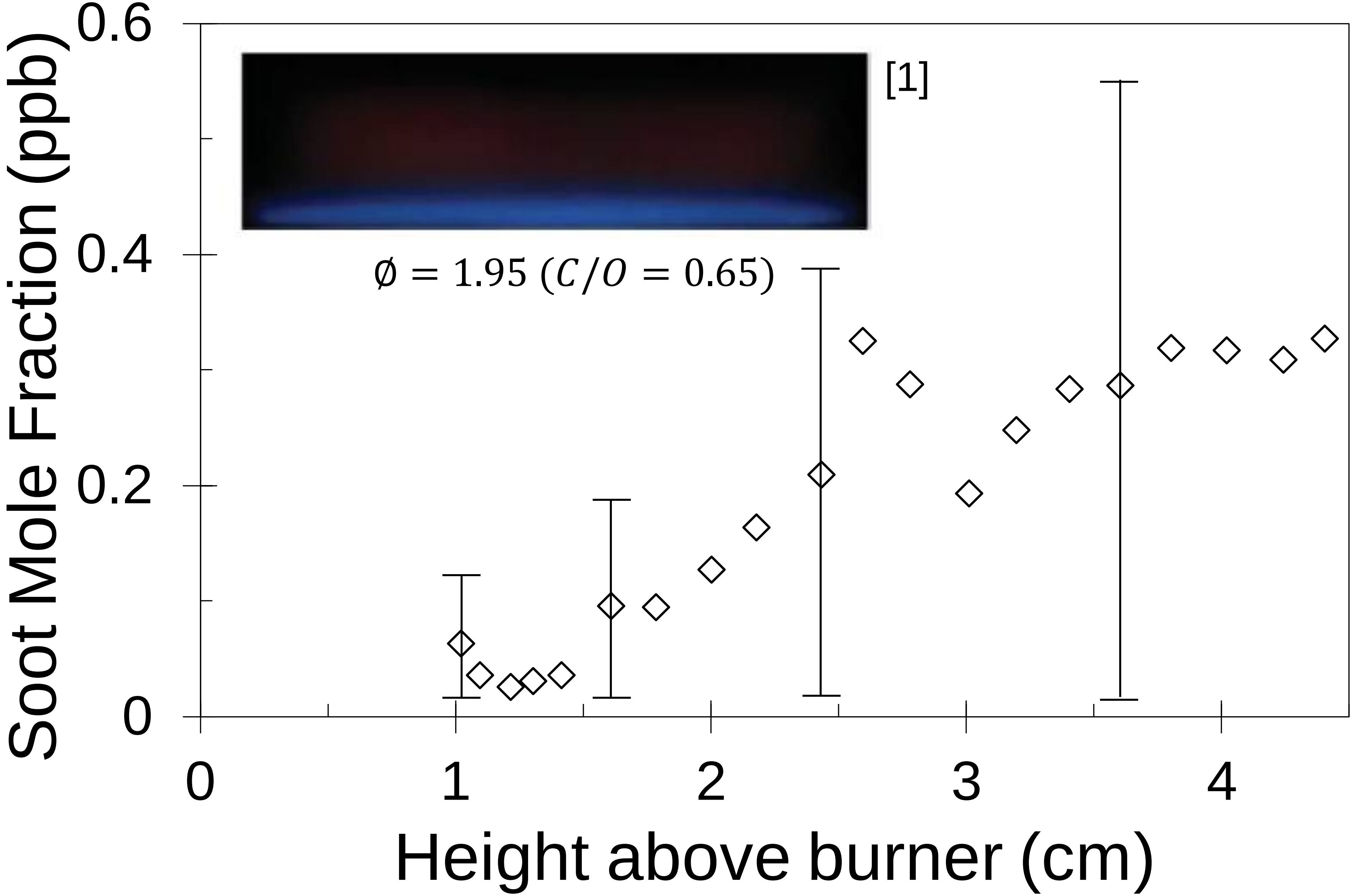



[2]

[1] Wang H*, P Combust Inst*, (2011), **33**, 41 .

[2] Violi A*, Combust Flame*, (2004), **139**, 279 .

Isolating Nucleation



Fuel+Ox

f_v ↑

$d_p = cons$

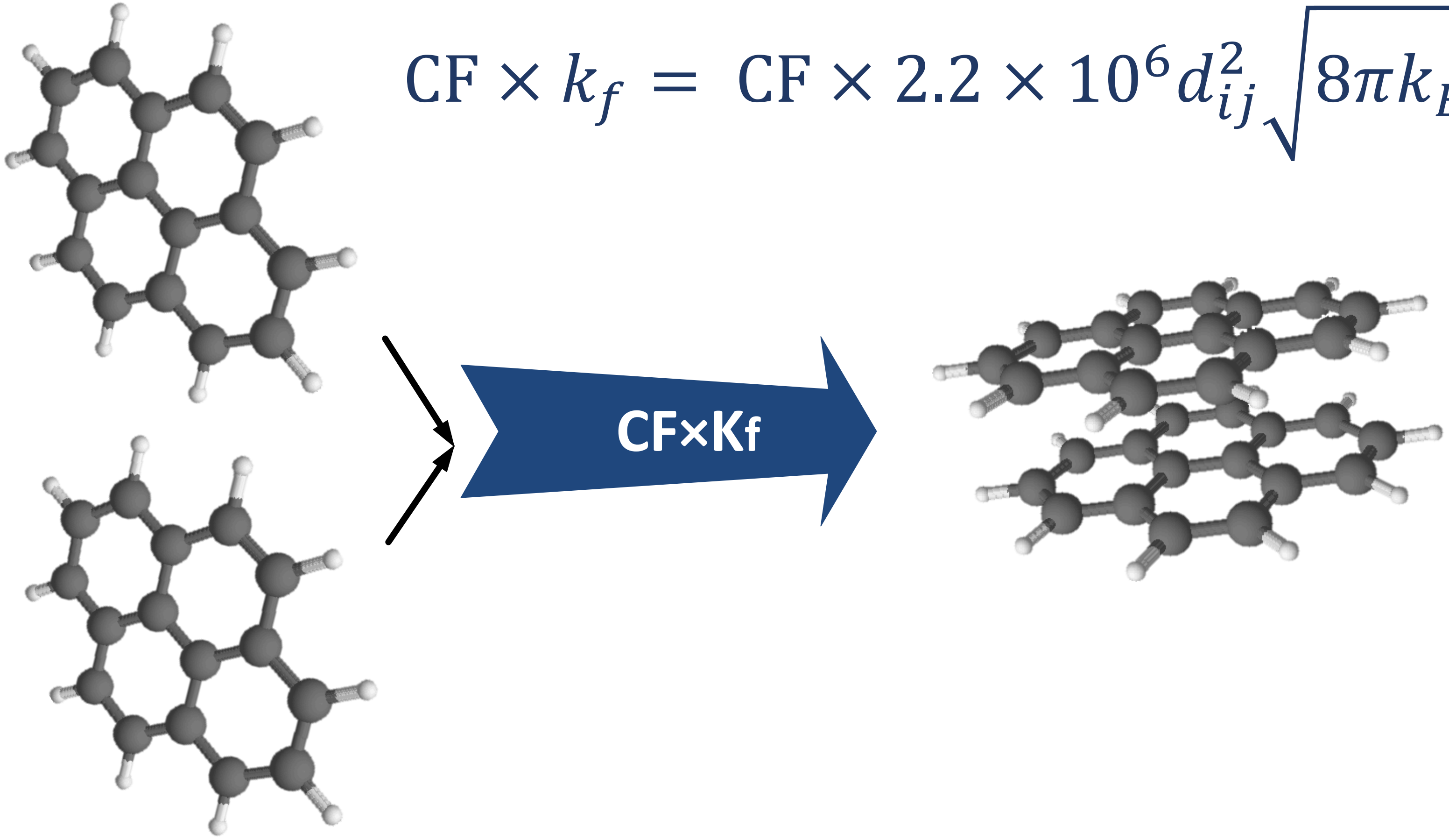
[2] Desgroux P, Faccinetto,A, Mercier M, Mouton T, Aubagnac Karkar D, El Bakali A, *Combust Flame*, (2017), **184**, 153 .

Irreversible Dimerization

the Classic Way

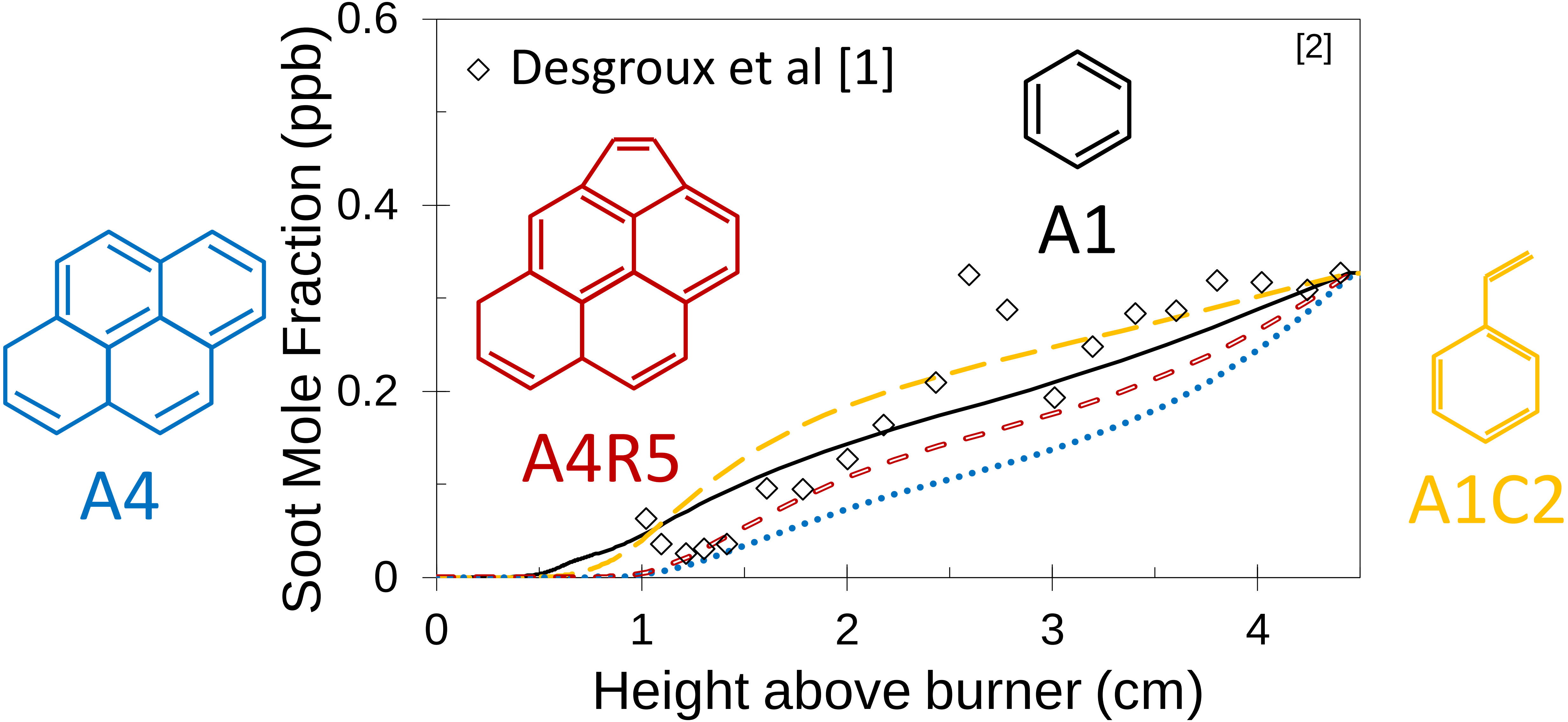
$$CF \times k_f = CF \times 2.2 \times 10^6 d_{ij}^2 \sqrt{8\pi k_B/\mu_{ij}}\, T^{0.5}$$

[1]



[1] Frenklach, M. and H. Wang, *Combust Flame*, (1991), **23**, 1559 .

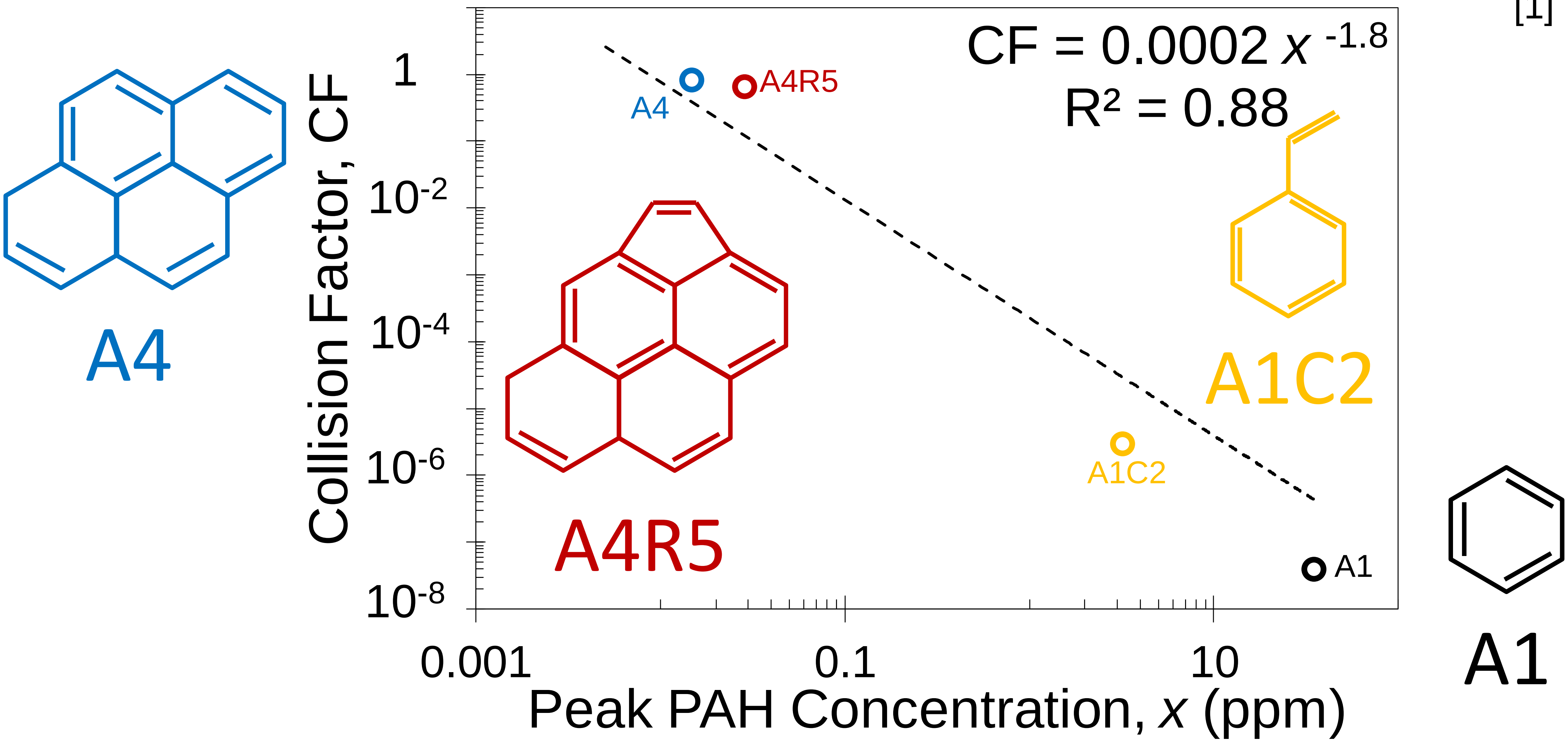
Pick a PAH, Tune CF, Get Good Results!



[1] Desgroux P, Faccinetto,A, Mercier M, Mouton T, Aubagnac Karkar D, El Bakali A, *Combust Flame*, (2017), **184**, 153 .
[2] Kholghy. M R, Kelesidis. G A, Pratsinis. S E, Phys. Chem. Chem. Phys, (2018), in press .

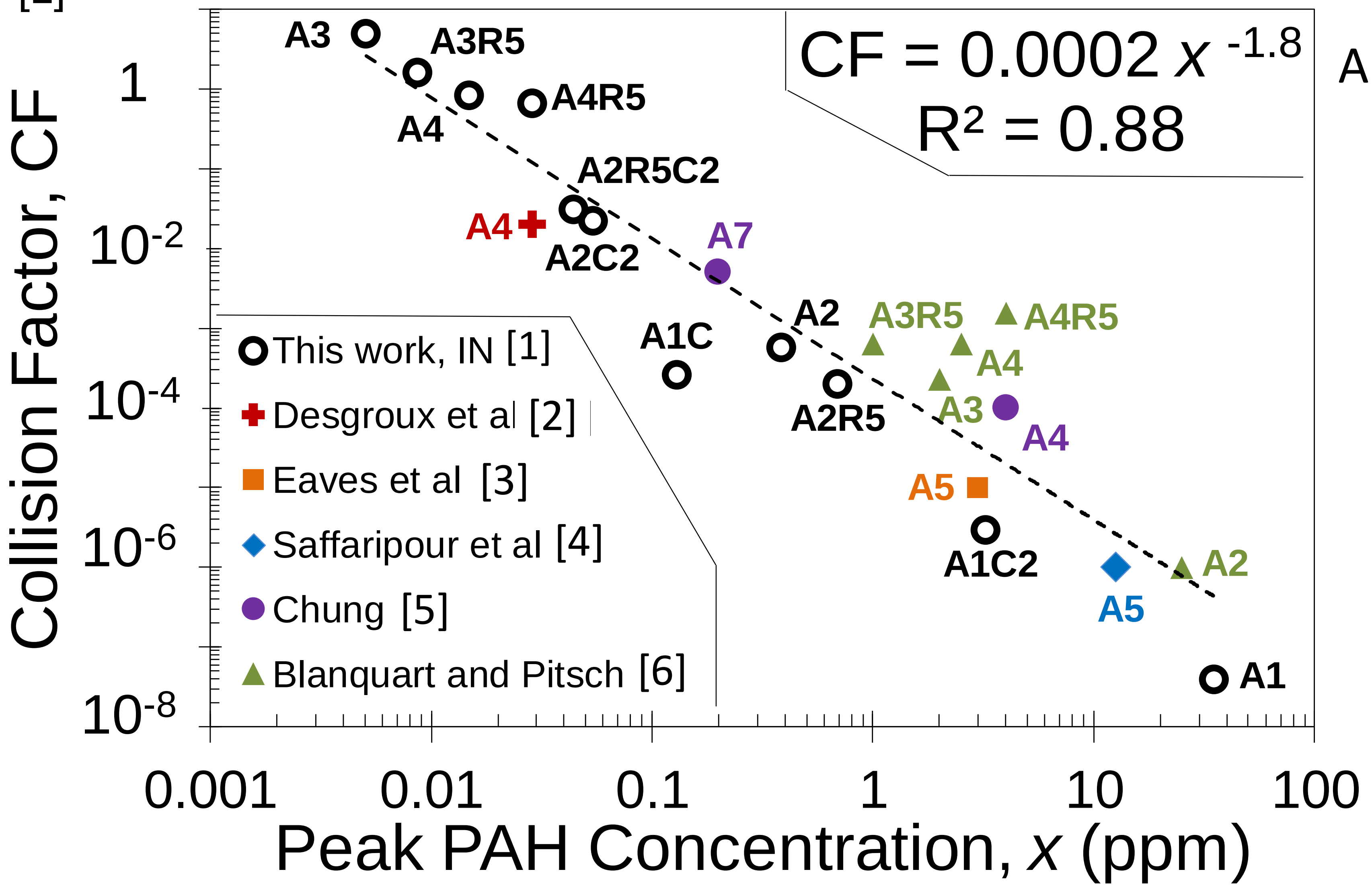
CF Varies by Orders of Magnitude

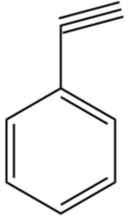
[1]

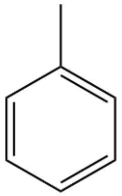


[1] Kholghy. M R, Kelesidis. G A, Pratsinis. S E, Phys. Chem. Chem. Phys, (2018), in press .

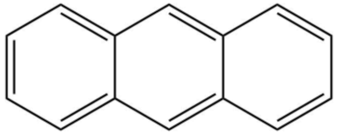
[1]

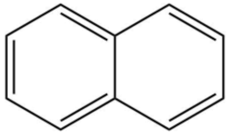


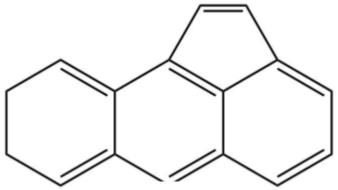
A1C2 

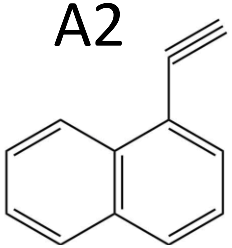
A1C 

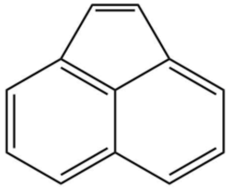
A1 

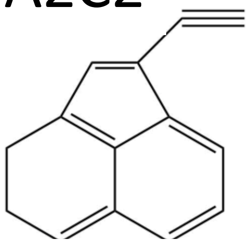

A3

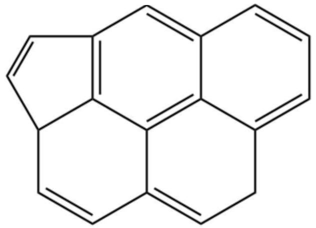

A2

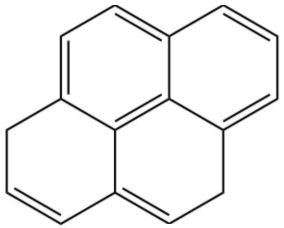

A3R5


A2C2


A2R5


A2R5C2


A4R5


A4

[1] Kholghy. M R, Kelesidis. G A, Pratsinis. S E, Phys. Chem. Chem. Phys, (2018), in press .

[2] Desgroux P, Faccinetto,A, Mercier M, Mouton T, Aubagnac Karkar D, El Bakali A, *Combust Flame*, (2017), **184**, 153 .

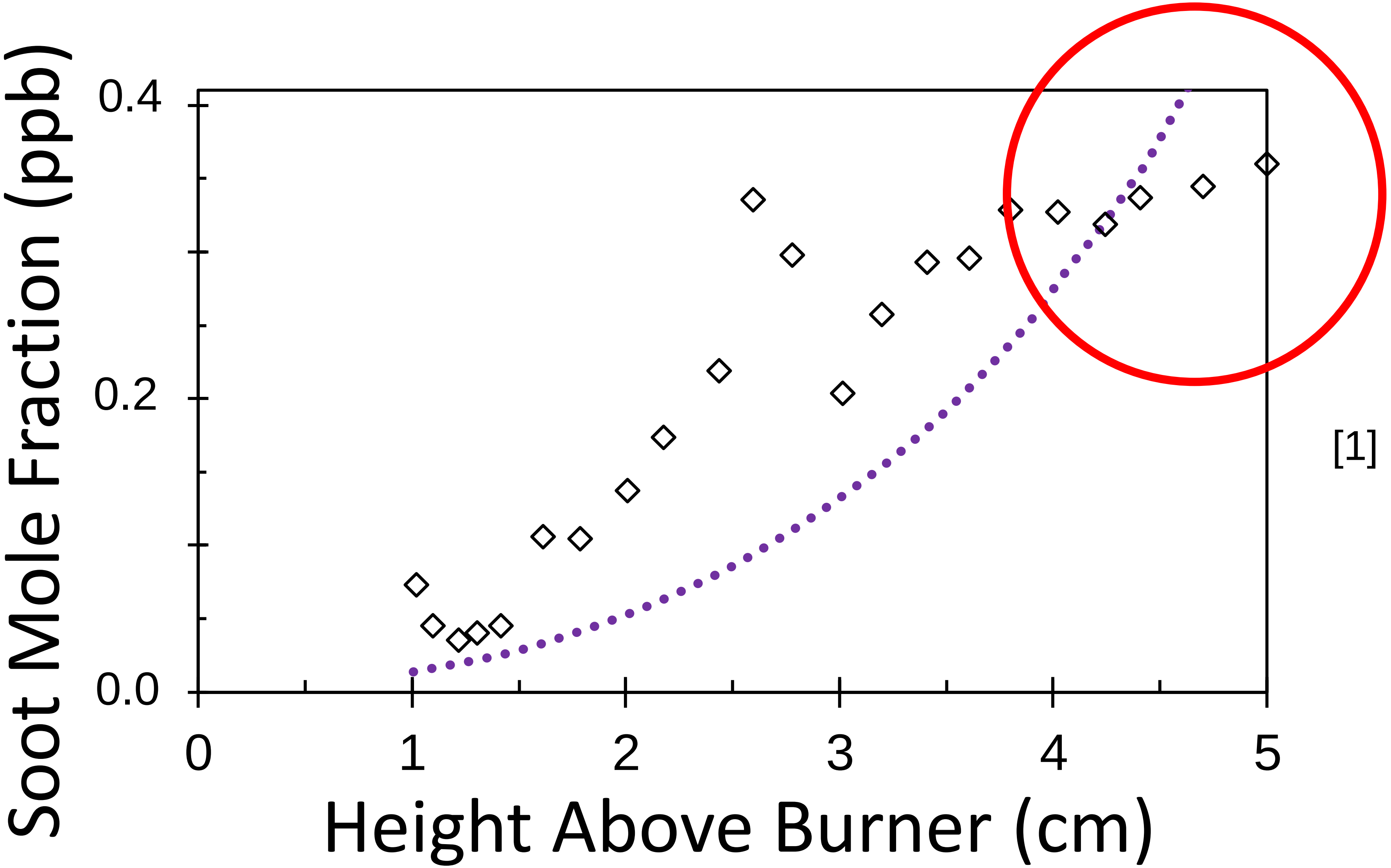
[3] Eaves. N A, Dworkin. S B, Thomson. M J, *P Combust Inst*, (2015), **35**, 1787 .

[4] Saffaripour, M., Veshkini, A., Kholghy, M., & Thomson, M. J. *Combustion and Flame*, (2014), *161*, 848

[5] Chung, S. H., & Violi, A. *P Combust Inst*, (2011) *33*, 693.

[6] Blanquart, G., & Pitsch, H. *Combust Flame,* (2009), *156*, 1614.

Does not capture temperature dependency



[1] Desgroux P, Faccinetto,A, Mercier M, Mouton T, Aubagnac Karkar D, El Bakali A, *Combust Flame*, (2017), **184**, 153 .

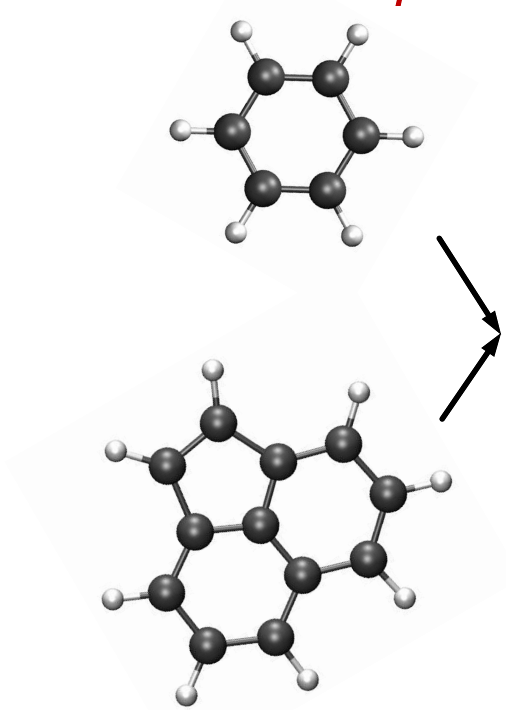
Reversible Dimerization

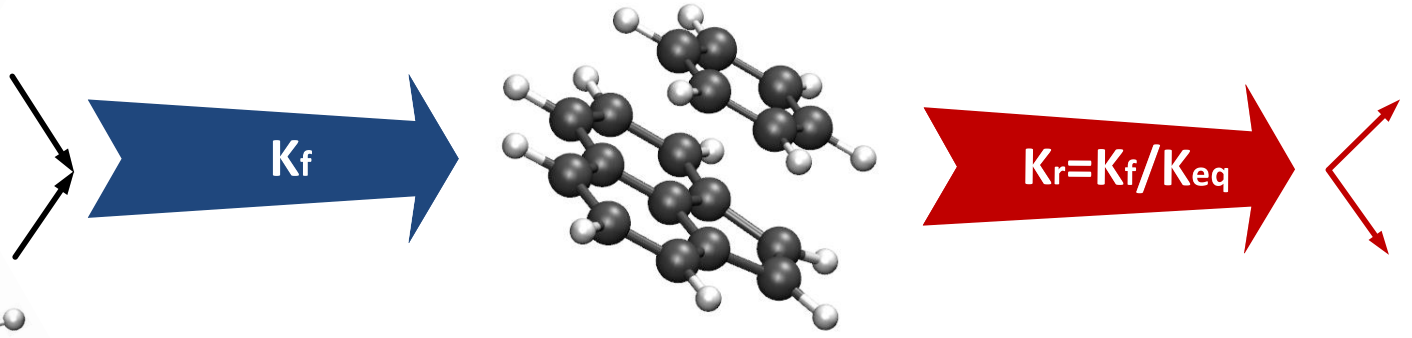
the Realistic Way

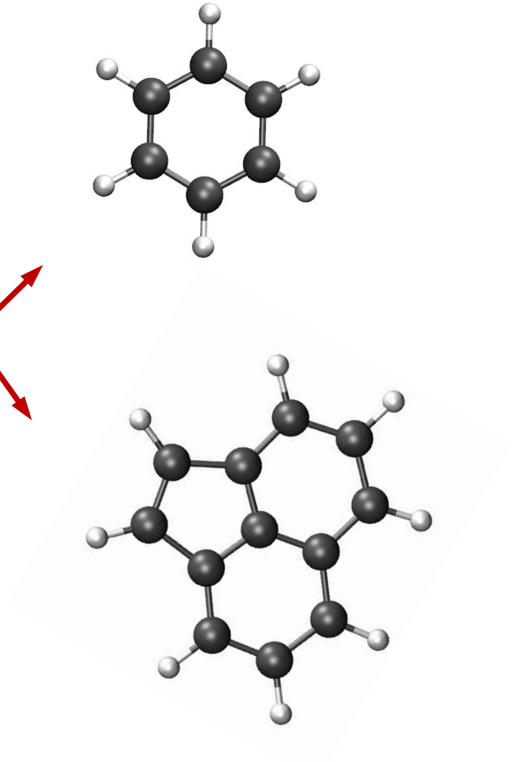
[1, 2]

$$k_f = 2.2\mathcal{P}10^6\, d_{ij}^2 \sqrt{8\pi k_B/\mu_{ij}}\, T^{0.5}$$ [3]

$$k_r = 2.2\mathcal{P}10^{6-b} d_{ij}^2 \sqrt{8\pi k_B/\mu_{ij}}\, T^{0.5} e^{(-a\varepsilon \ln b/R_u T)}$$



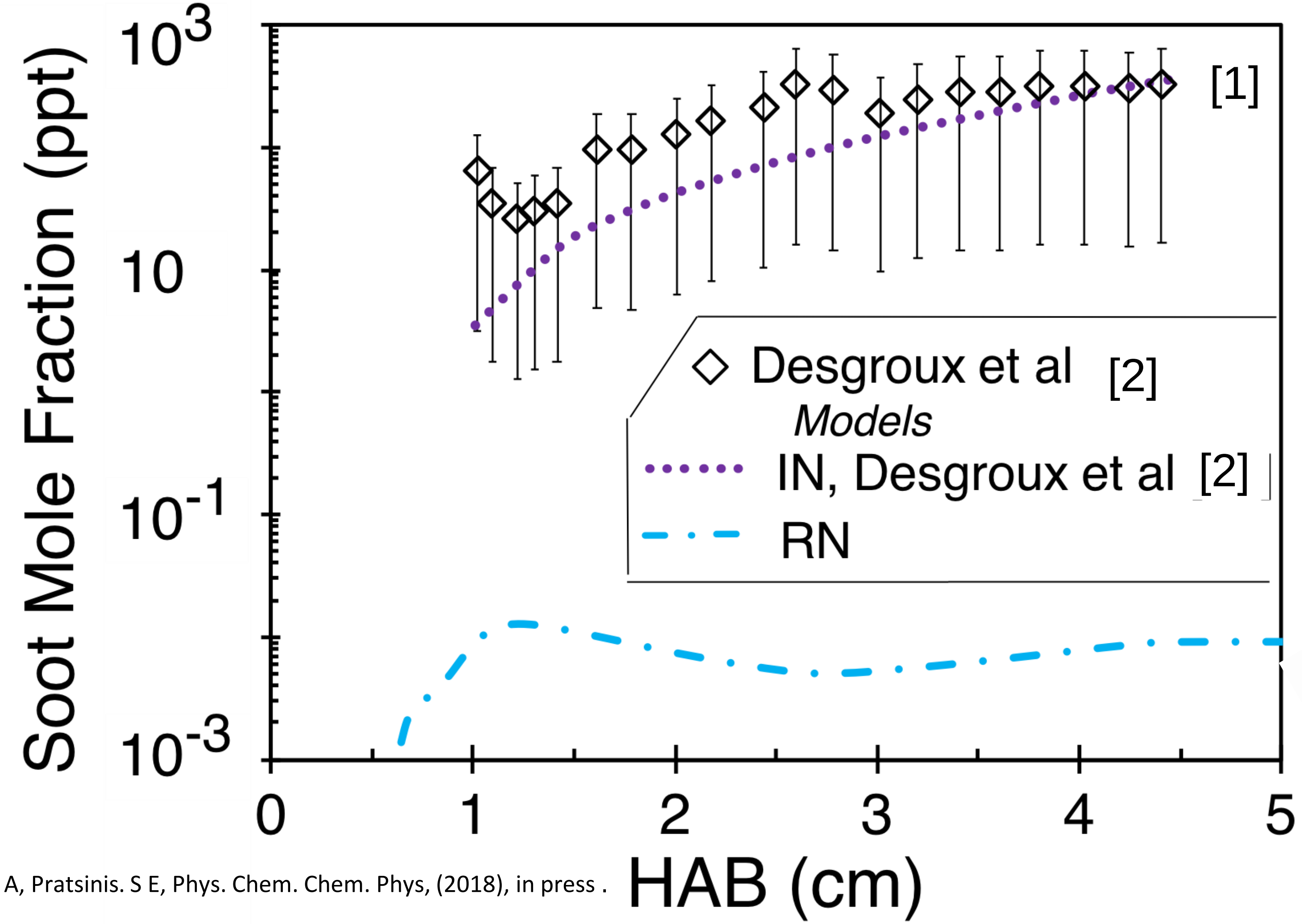


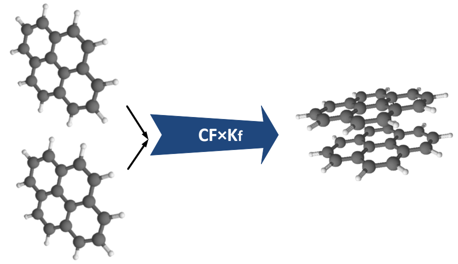


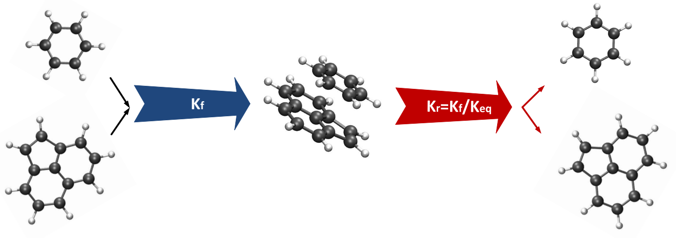
$$\log_{10} k_{eq} = a\frac{\varepsilon}{R_u T} + b \qquad \varepsilon = c\, MW_{ij} - d$$

[1] Eaves. N A, Dworkin. S B, Thomson. M J, *P Combust Inst*, (2015), **35**, 1787 .
[2] Miller. H J, *P Combust Inst*, (1990), **23**, 91 .
[3] Kholghy. M R, Kelesidis. G A, Pratsinis. S E, Phys. Chem. Chem. Phys, (2018), in press .

But, @ 1800 K, Most Dimers Separate





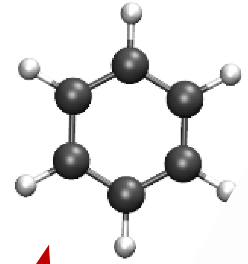


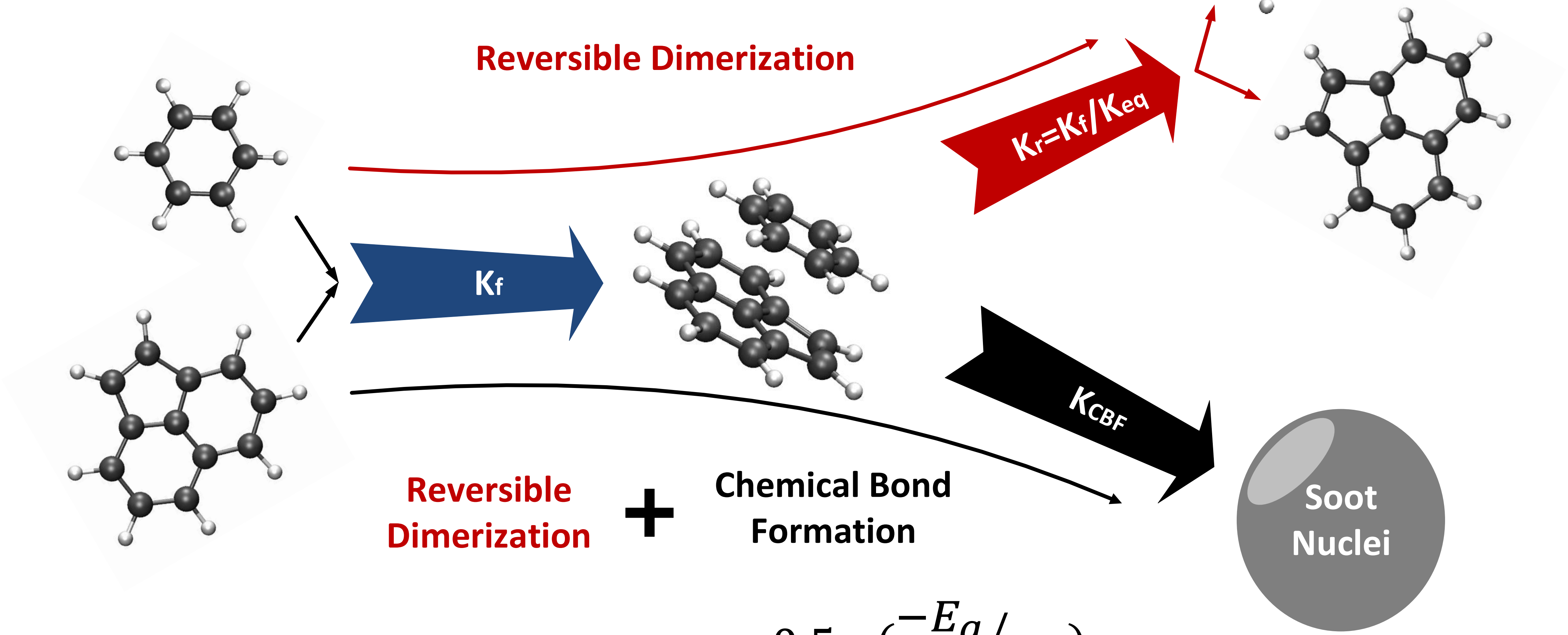
[1] Kholghy. M R, Kelesidis. G A, Pratsinis. S E, Phys. Chem. Chem. Phys, (2018), in press .

[2] Desgroux P, Faccinetto,A, Mercier M, Mouton T, Aubagnac Karkar D, El Bakali A*, Combust Flame*, (2017), **184**, 153 .

Reactive PAH Dimerization

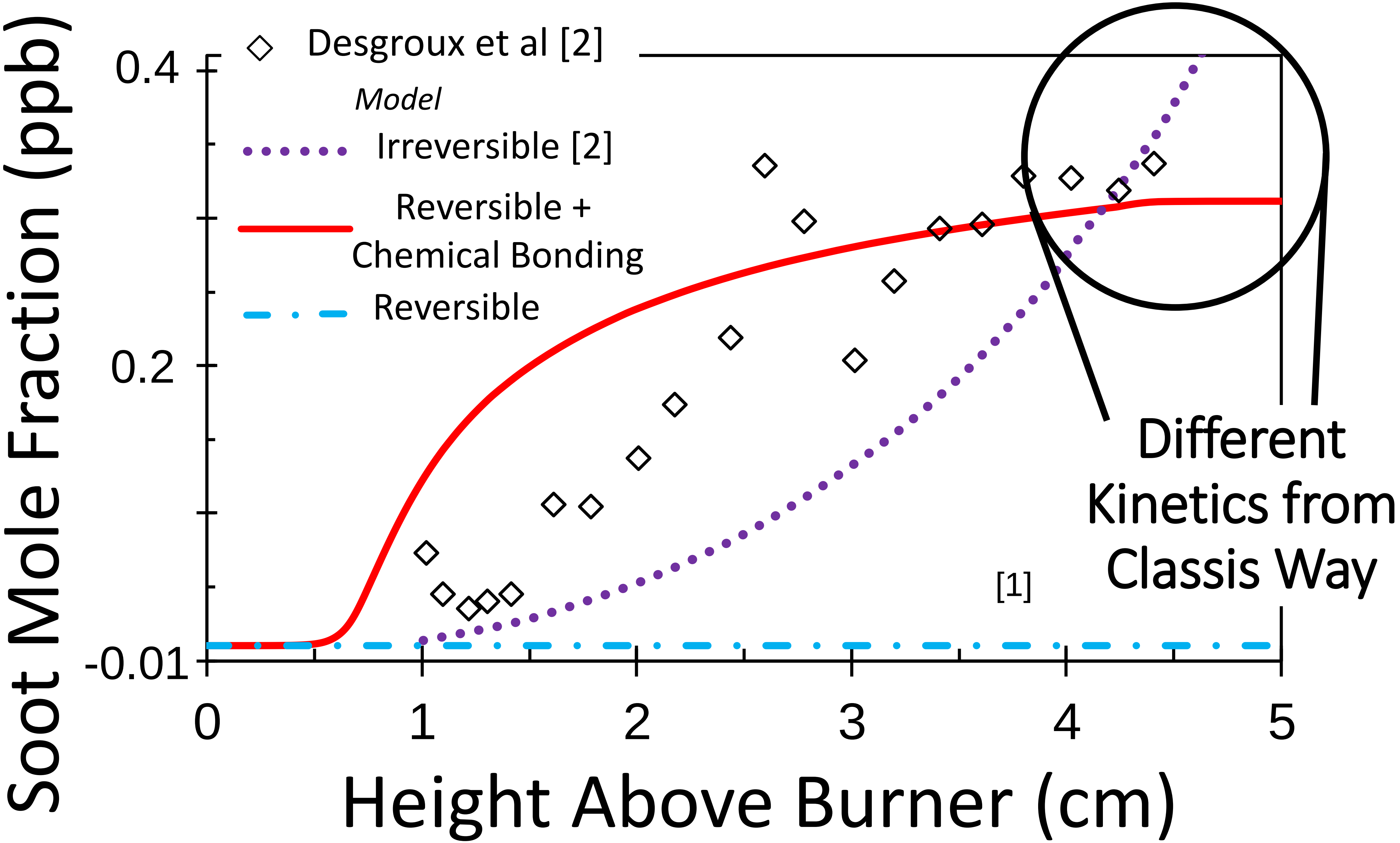
this work





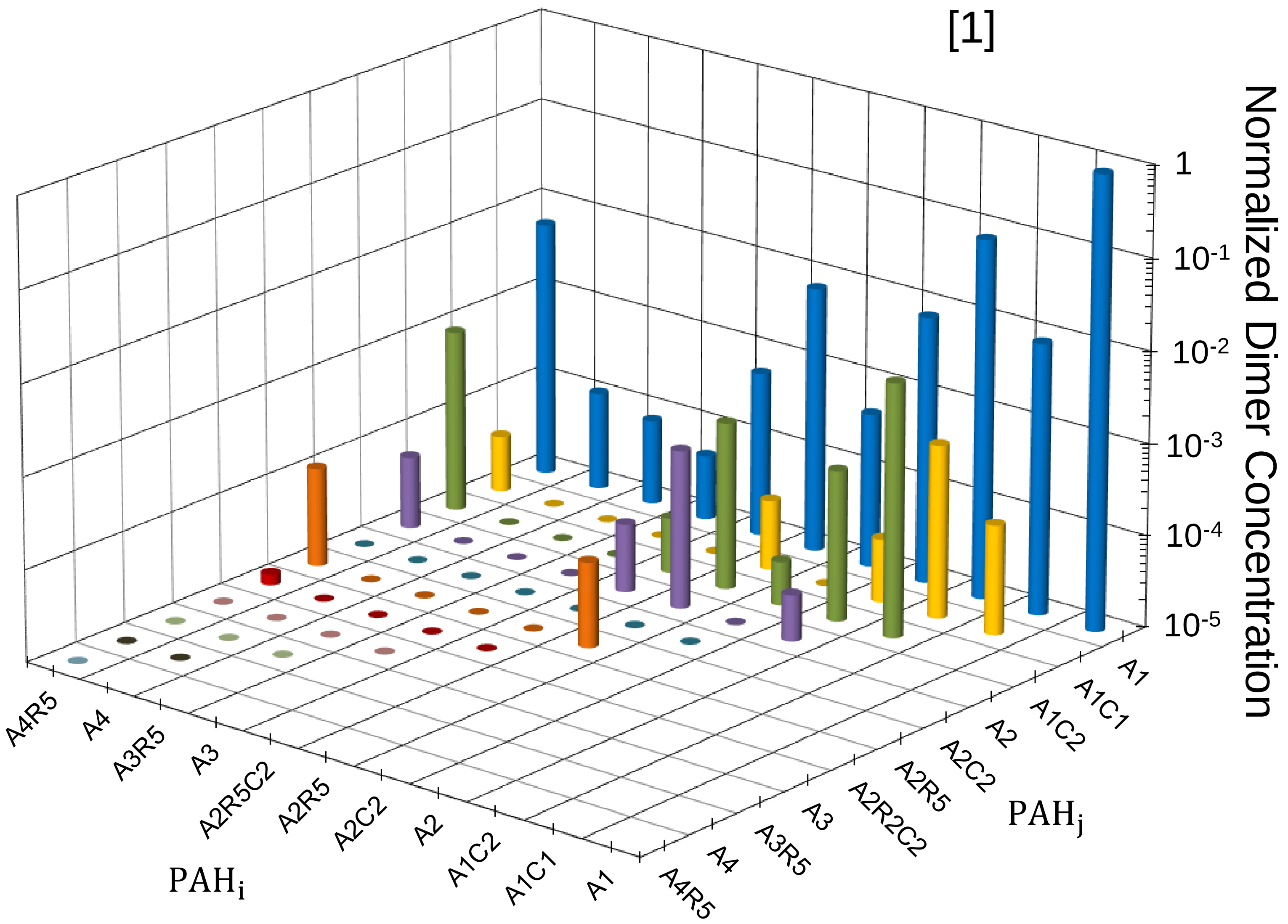
$$k_{CBF} = A\ T^{0.5} e^{\left(-E_a/_{RT}\right)}$$

[1] Kholghy. M R, Kelesidis. G A, Pratsinis. S E, Phys. Chem. Chem. Phys, (2018), in press .



[1] Kholghy. M R, Kelesidis. G A, Pratsinis. S E, Phys. Chem. Chem. Phys, (2018), in press .
[2] Desgroux P, Faccinetto,A, Mercier M, Mouton T, Aubagnac Karkar D, El Bakali A*, Combust Flame*, (2017), **184**, 153 .

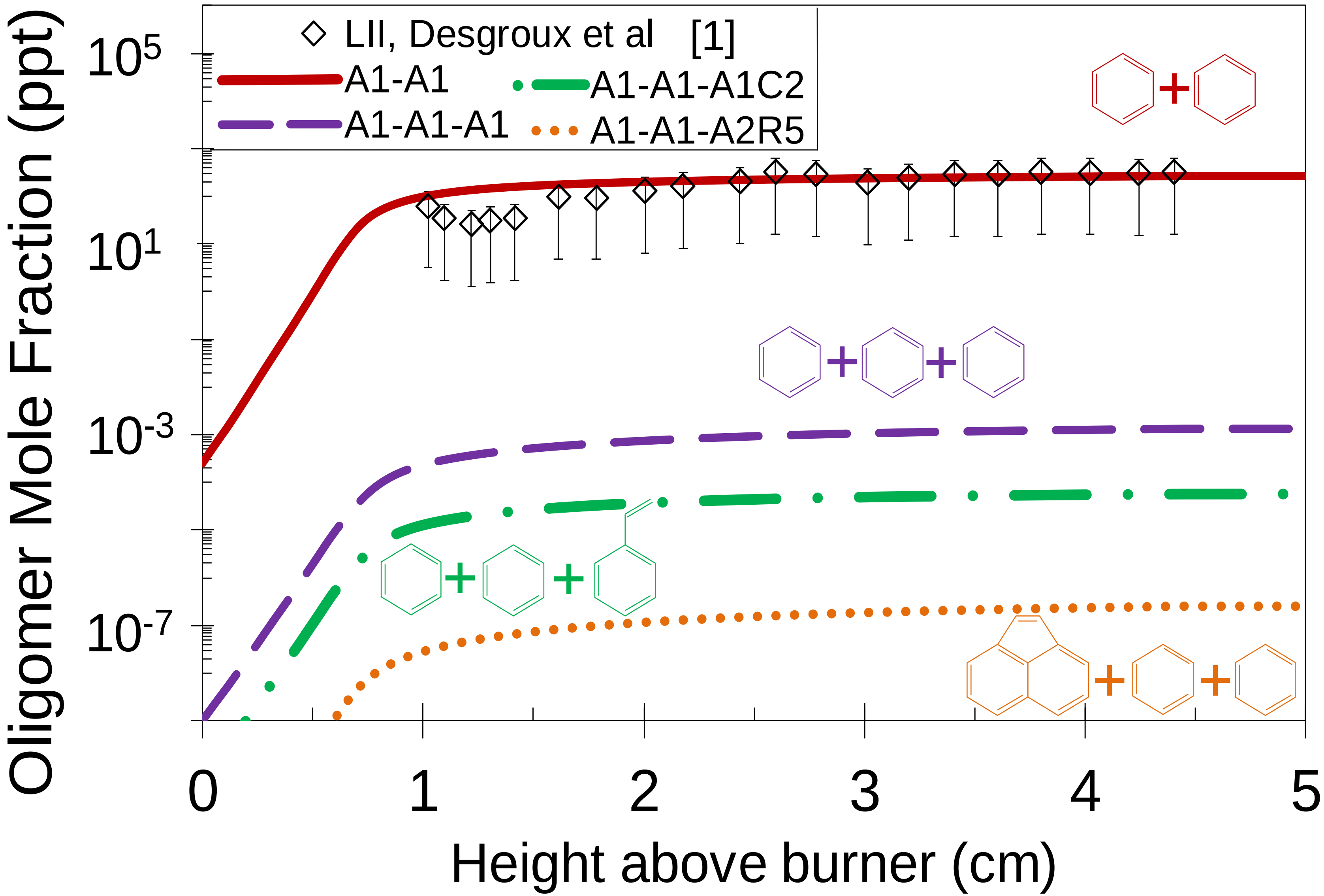
Most Dimers Come from Small Aromatics



[1] Kholghy. M R, Kelesidis. G A, Pratsinis. S E, Phys. Chem. Chem. Phys, (2018), in press .

Dimer are Dominant

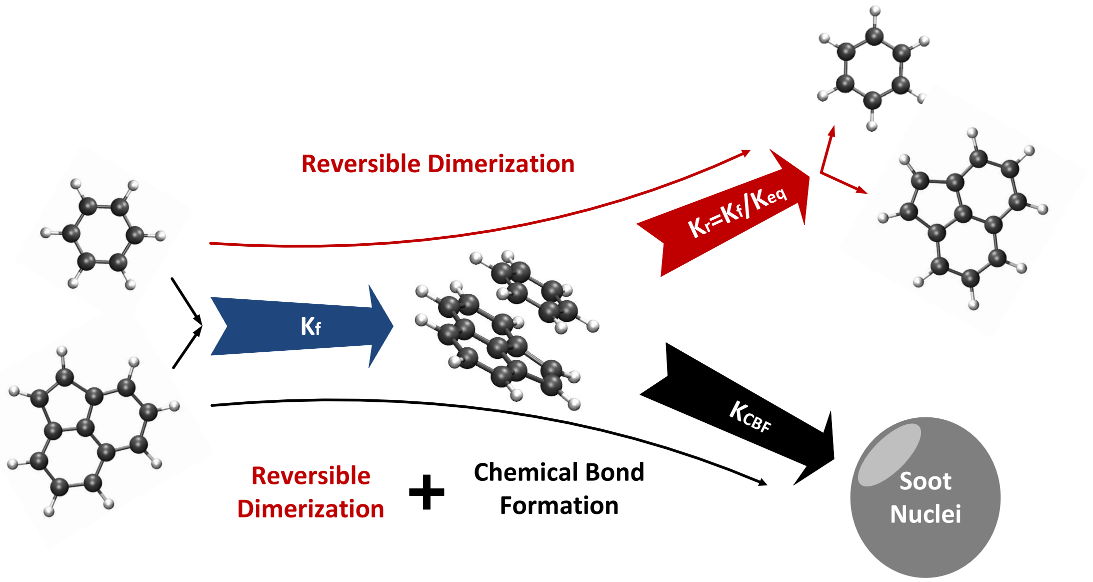
[2]



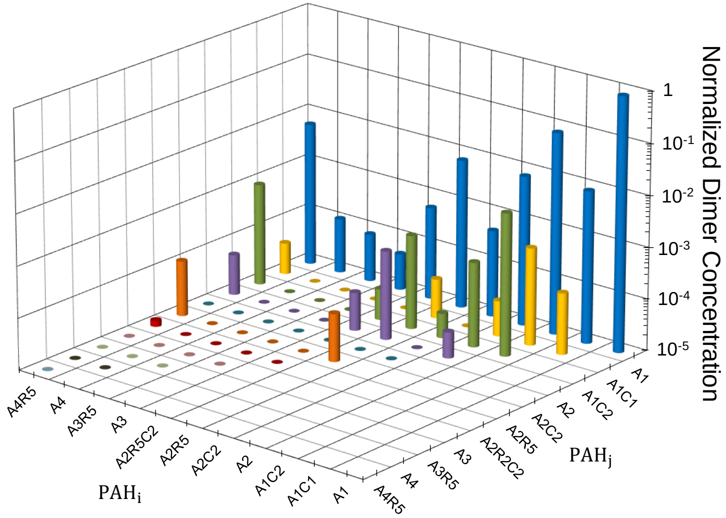
[1] Desgroux P, Faccinetto,A, Mercier M, Mouton T, Aubagnac Karkar D, El Bakali A*, Combust Flame*, (2017), **184**, 153 .

[2] Kholghy. M R, Kelesidis. G A, Pratsinis. S E, Phys. Chem. Chem. Phys, (2018), in press .

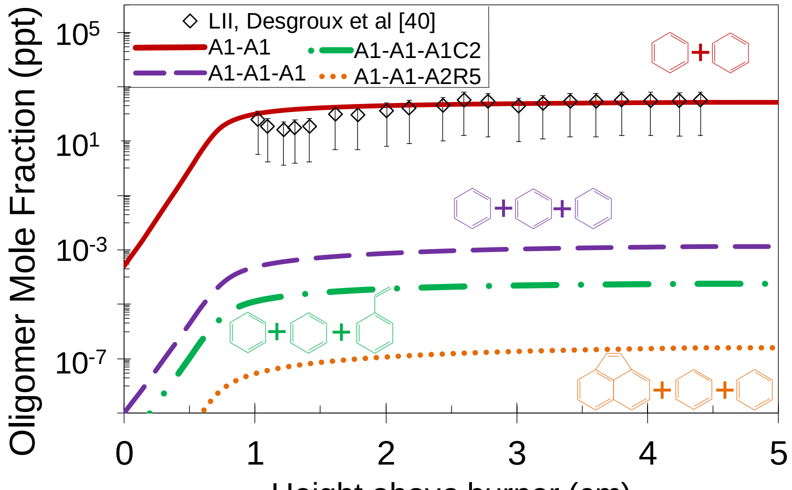
Conclusions



- Soot nucleation must involve strong chemical bonds between PAHs



- Small Aromatics/PAHs contribute the most to soot nucleation



- Dimers are the main oligomers of incipient soot

Thank you for your attention

Full story in:

Kholghy, M. R, Kelesidis, G. A, Pratsinis, G. A,
"Reactive polycyclic aromatic hydrocarbon dimerization drives soot nucleation", *Physical Chemistry Chemical Physics* 20.16 (2018): 10926-10938