



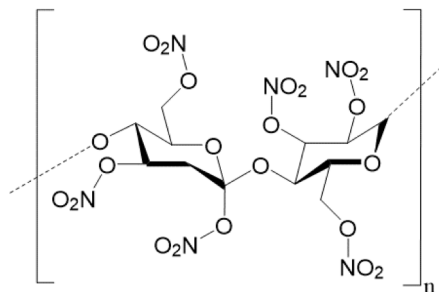
# **Accounting for super-, plateau- and mesa-rate burning by lead and copper-based ballistic modifiers in double-base propellants: a computational study**

9<sup>th</sup> International Nitrocellulose Symposium

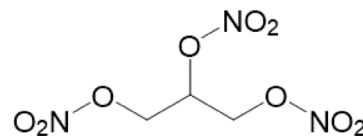
June 2023

**Lisette Warren**, Aaron Rowell, Patrick McMaster,  
Colin Pulham and Carole Morrison

# What does a ballistic modifier do?

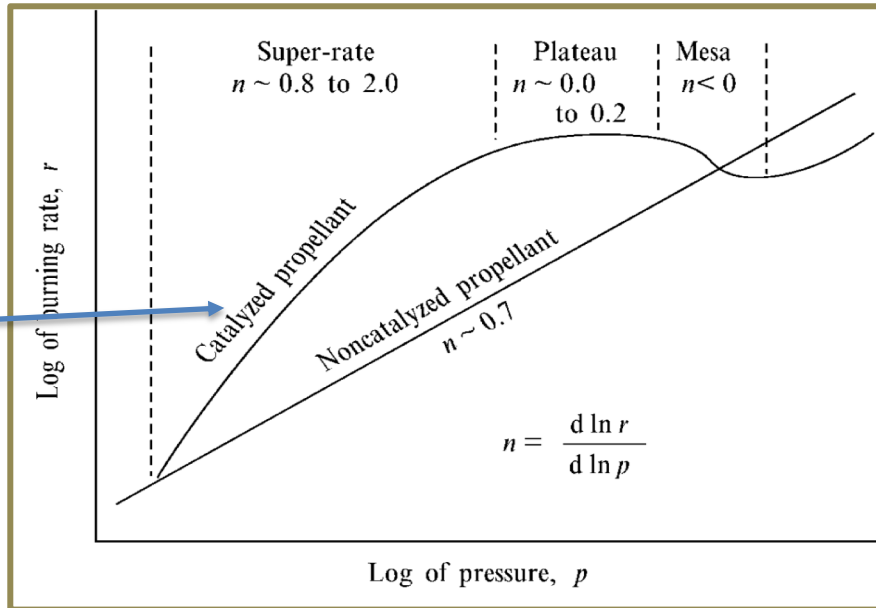


Nitrocellulose  
Energetic polymer



Nitroglycerin  
Energetic plasticizer

Lead salts

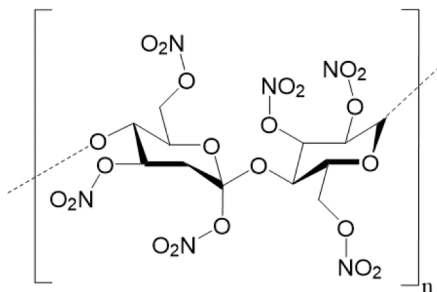


Burn rate vs pressure graph [1]

[1] N. Kubota *et al. Symp. Combust.*, 1975, **15**, 529–537

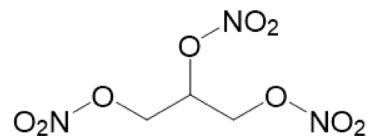


# What does a ballistic modifier do?



Nitrocellulose  
Energetic polymer

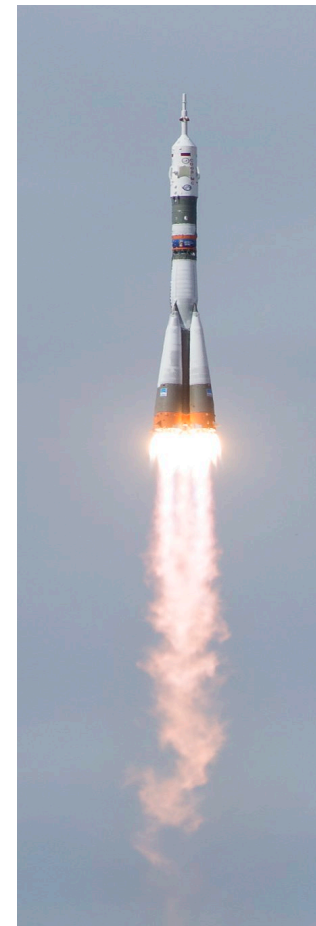
+



Nitroglycerin  
Energetic plasticizer



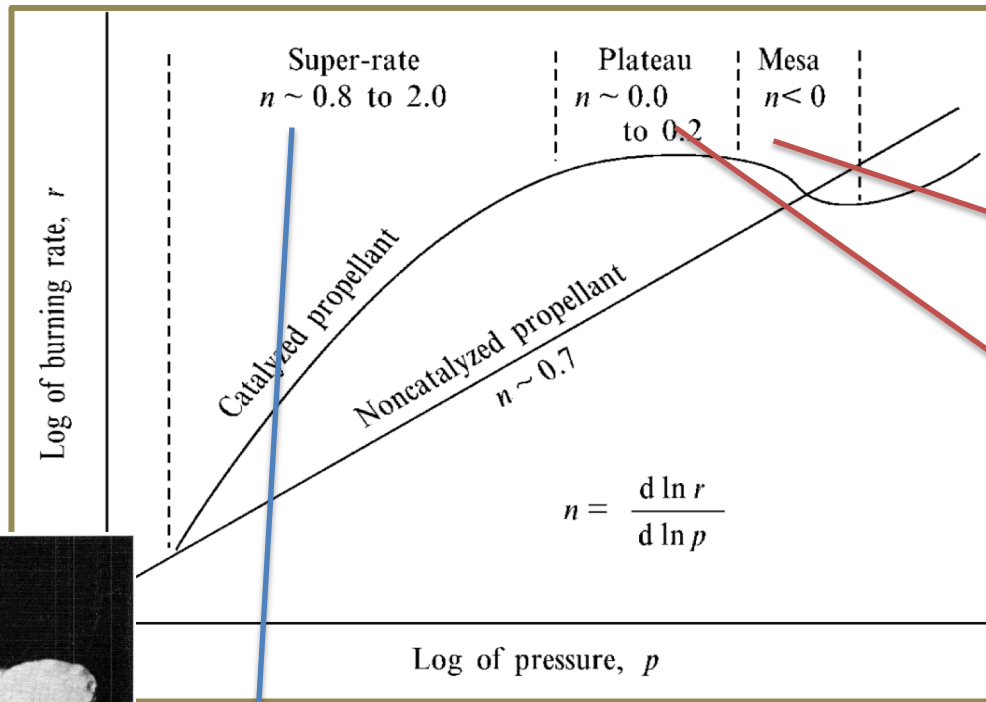
Dependence on lead remains current today



[1] Lead REACH Consortium, <https://ila-reach.org/>.

[2] D. J. Hewkin *et al.* *Combust. Sci. Technol.*, 1971, **2**, 307–327

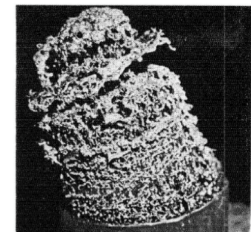
# Carbon soot theory



Burn rate vs pressure graph [3]

1. In presence of lead, carbon matrix formation occurs [1-4]

3. Plateau/ mesa burning :  
loss of Pb/C catalyst with  
pressure increase [1-4]  
UNIQUE TO Pb.

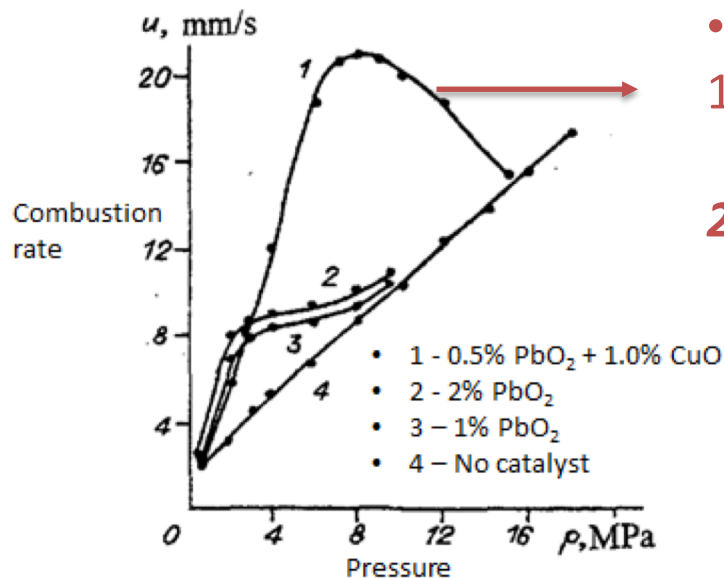


2. Super rate: formation of Pb/C matrix [1-4]

- [1] L. R. Warren *et al. Prop., Explos., Pyrotech.* **2021**, *46*, 13.
- [2] D. J. Hewkin *et al. Combust. Sci. Technol.*, 1971, **2**, 307–327
- [3] N. Kubota *et al. Symp. Combust.*, 1975, **15**, 529–537
- [4] C. Youfang, *Propellants, Explos. Pyrotech.*, 1987, **12**, 209–214.

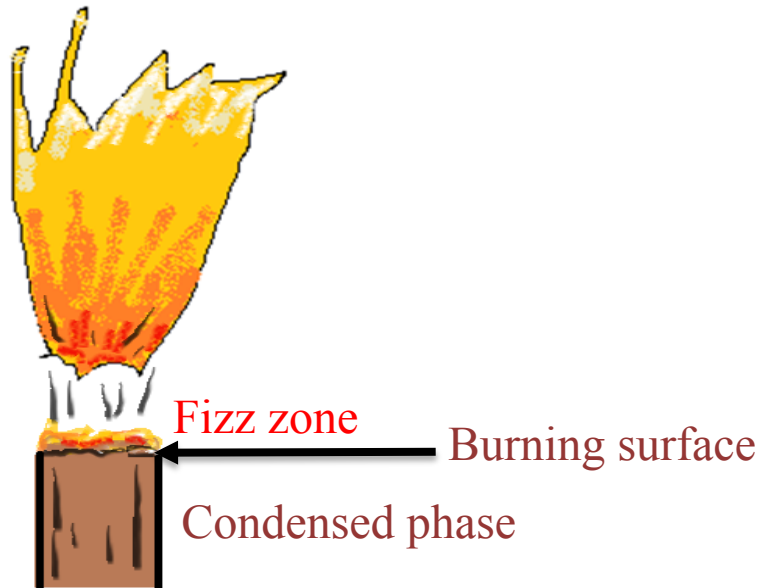
## Ballistic modifiers: Pb and Cu

- Account for difference in burn rate profile observed with Pb and Cu salts added to DBPs



- Addition of copper oxide:
  - Propels super-rate burning to much higher pressures
  - Plateau burning transitions to mesa burning

# How to model a propellant?



Solid gas interface<sup>1,2</sup>  
Two models

Split into:

- Solid-state study<sup>3</sup>
- Gas phase study

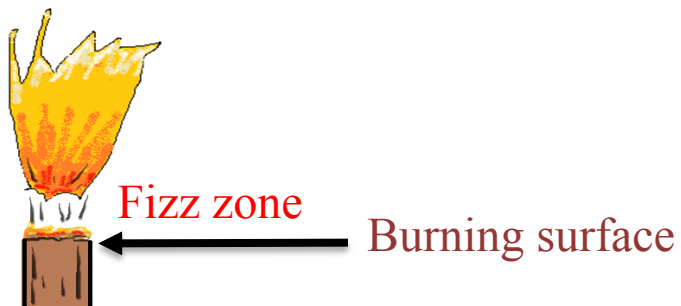
Fundamental assumption:

- Under burning surface temperature conditions  
~ 300 °C<sup>4</sup>

Ballistic modifier decomposes to metal oxide<sup>5</sup>

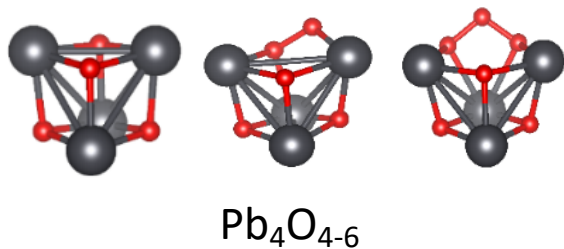
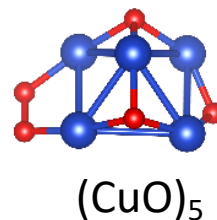
1. N. P. Suh *et al.*, *Combust. Flame*, 1974, **22**, 289–293.
2. L. R. Warren *et al.*, *Propellants, Explos. Pyrotech.*, 2021, **46**, 13–25.
3. L.R. Warren *et al.* *PCCP.*, 2020, **22**, 25502–25513
4. G. Lengellé *et al.*, *Symp. Combust.*, 1977, **16**, 1257–1269.
5. H. Singh *et al.*, *Proc. Indian. Acad. Sci*, 1984, **93**, 93–97.

# Modelling the fizz zone



- Non-equilibrium conditions of combustion flame- where to start on cluster size and stability?

Experiments suggest investigate metal oxide library of structures up to  $M_6$  with oxygen variation [1-3]

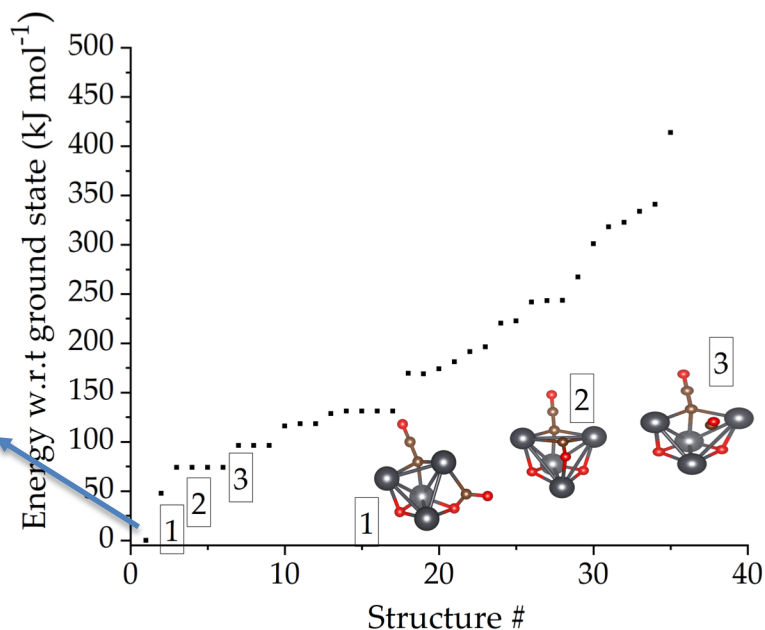
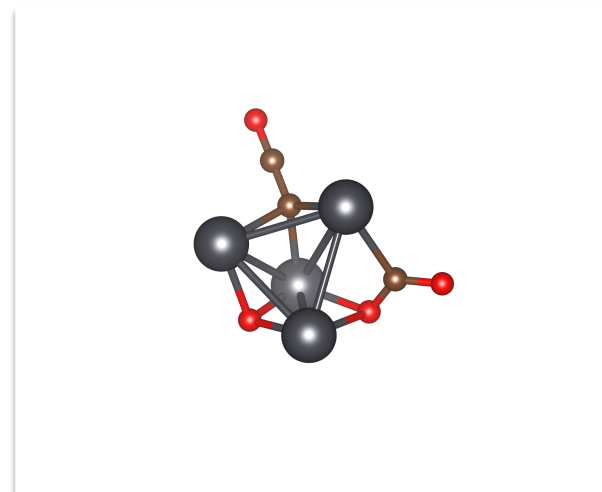


- [1] A. T. Benjelloun *et al.* *J. Chem. Phys.*, 2005, **122**, 154304.  
 [2] J. Drowart *et al.* *Trans. Faraday Soc.*, 1965, **61**, 1376–1383  
 [3] H. Liu *et al.* *J. Chem. Phys.*, 2007, **126**, 134705.

Colour scheme: red (O), dark grey (Pb), blue (Cu)

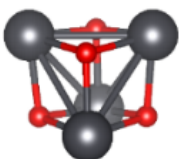
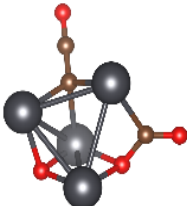
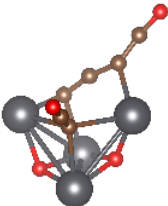
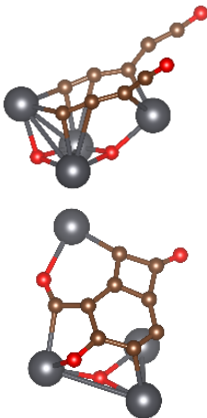
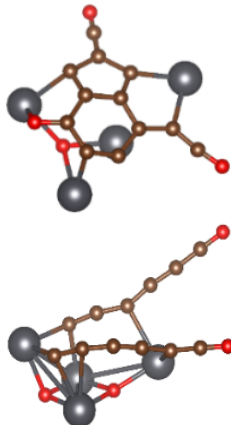
# Methods: structure searching

- Ab initio random structure searching (AIRSS)
- Metal oxide structure + random C atoms
- Geometry optimisation (DFT)
- Rank resulting structures by energy
- Investigate trends in low energy structures



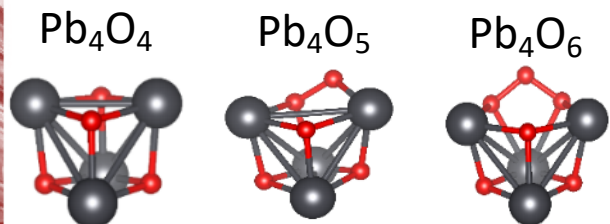
Colour scheme: red (O), dark grey (Pb), gold (C)

# Carbon addition to lead oxide clusters

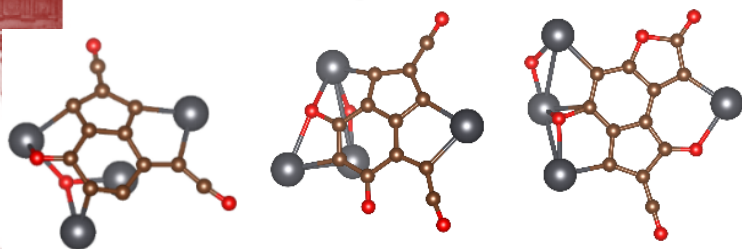
| Cluster                            | +0C                                                                               | + 3C                                                                              | + 6C                                                                               | + 9C                                                                                 | + 12C                                                                                |
|------------------------------------|-----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|
| <b>Pb<sub>4</sub>O<sub>4</sub></b> |  |  |  |  |  |
|                                    |                                                                                   |                                                                                   |                                                                                    | (+2 kJ mol <sup>-1</sup> )                                                           | (+140 kJ mol <sup>-1</sup> )                                                         |

Colour scheme: red (O), dark grey (Pb), gold (C)

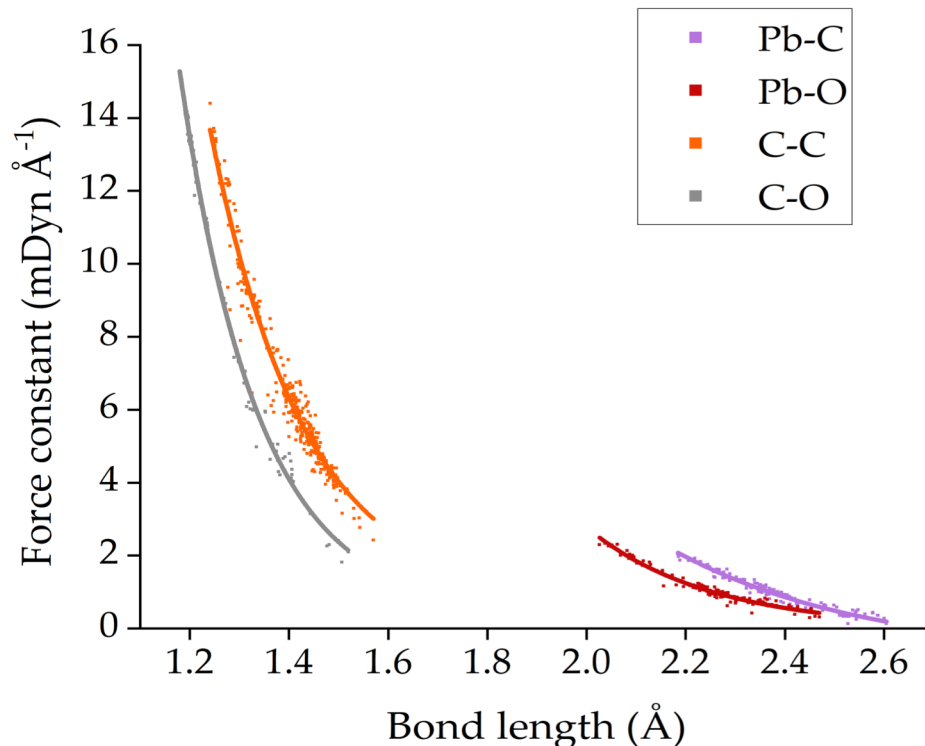
# Carbon addition to lead oxide clusters



FORMS AROMATIC CARBON

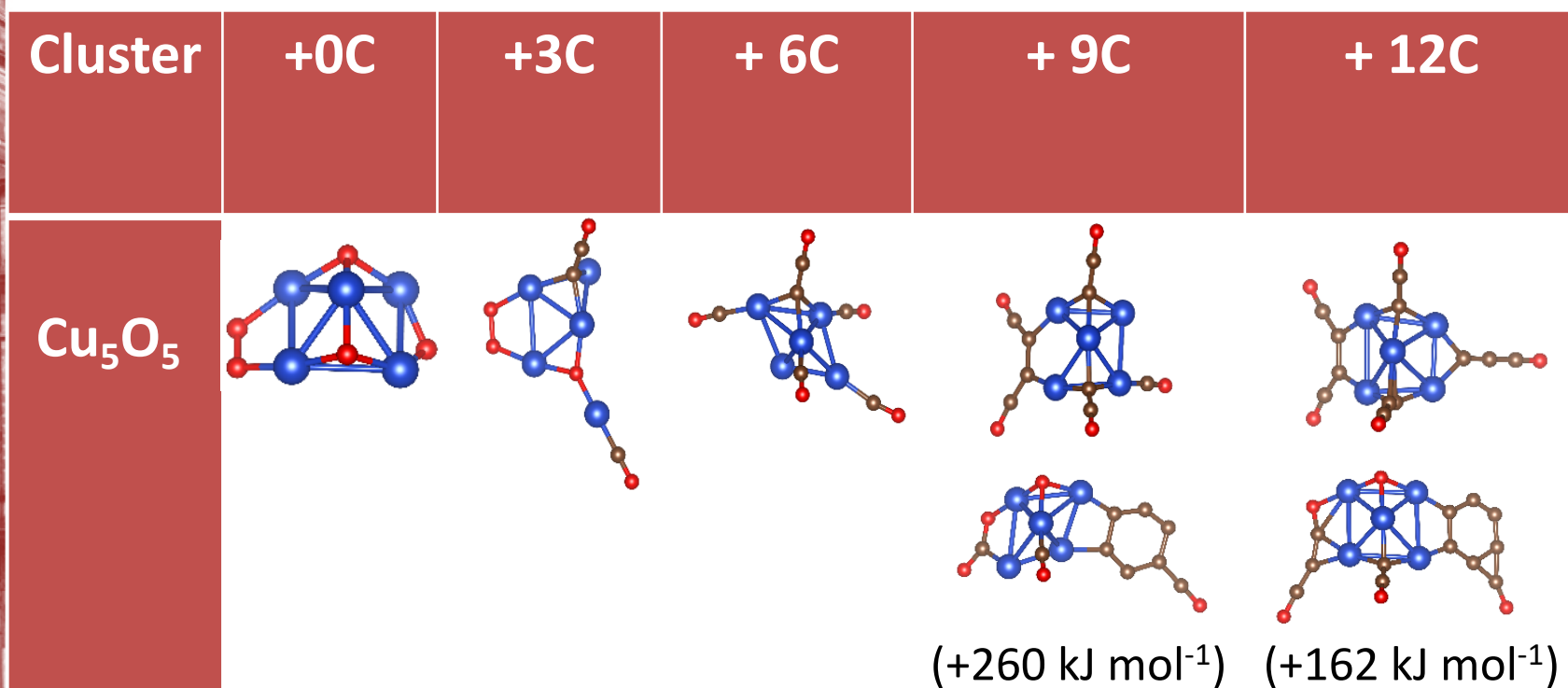


Colour scheme: red (O), dark grey (Pb), gold (C)



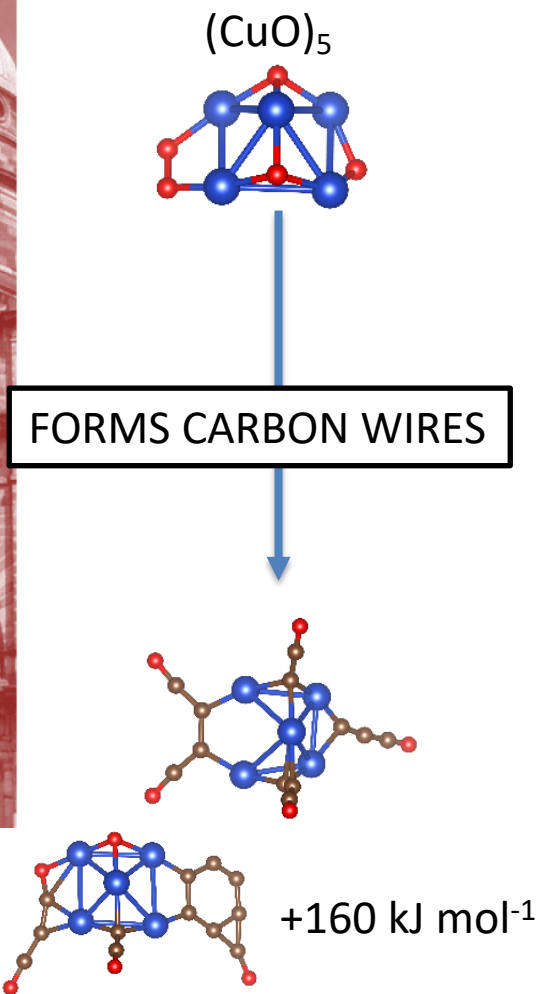
[1] E. Kraka *et al.*, *WIREs Comput. Mol. Sci.*, 2020, **10**, 1480.

# Carbon addition to copper oxide clusters

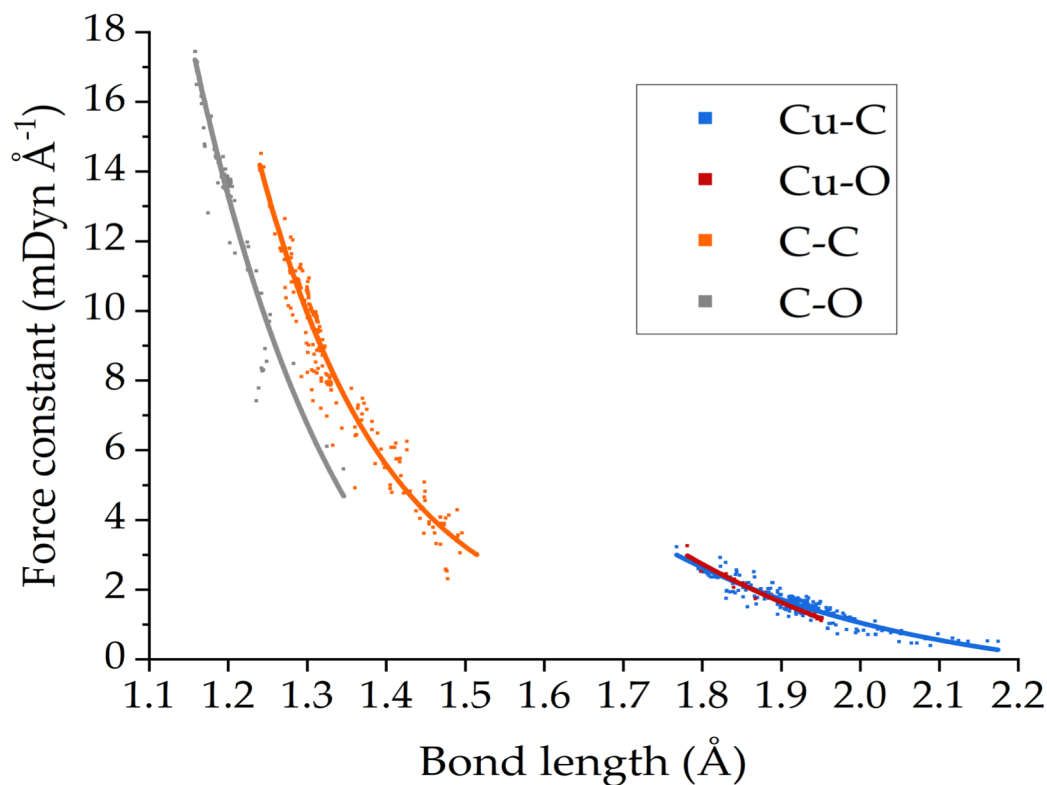


Colour scheme: red (O), gold (C), blue (Cu)

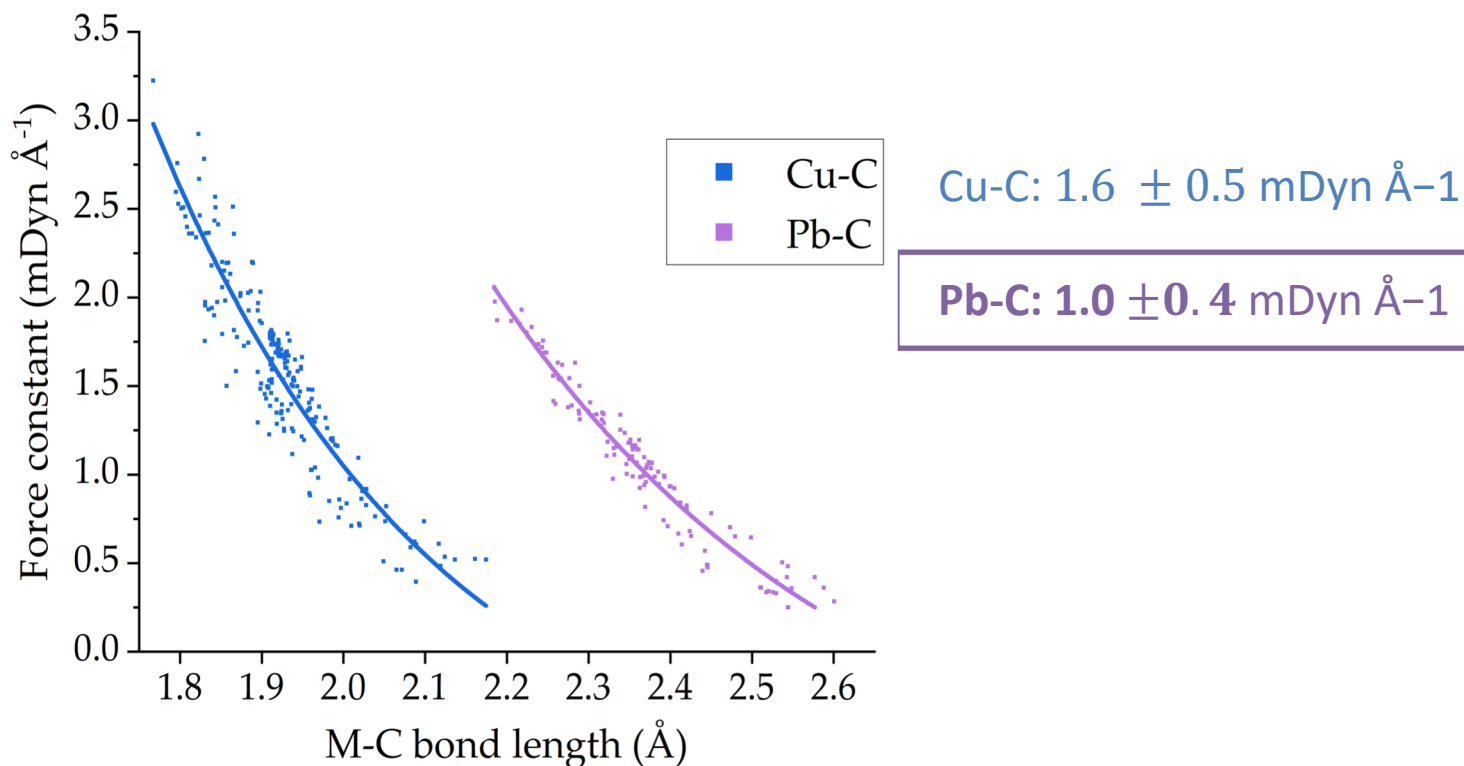
# Carbon addition to copper oxide clusters



Colour scheme: red (O), gold (C), blue (Cu)



# Carbon soot theory: M-C bond strength



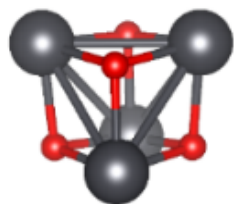
# Chemical reactivity within combustion flame



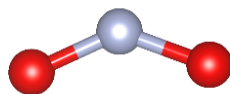
Fizz zone

Burning surface

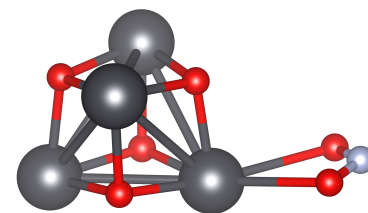
Investigate NO<sub>2</sub> binding to metal oxide cluster (with carbon)



$E(\text{cluster})$



$E(\text{molecule})$

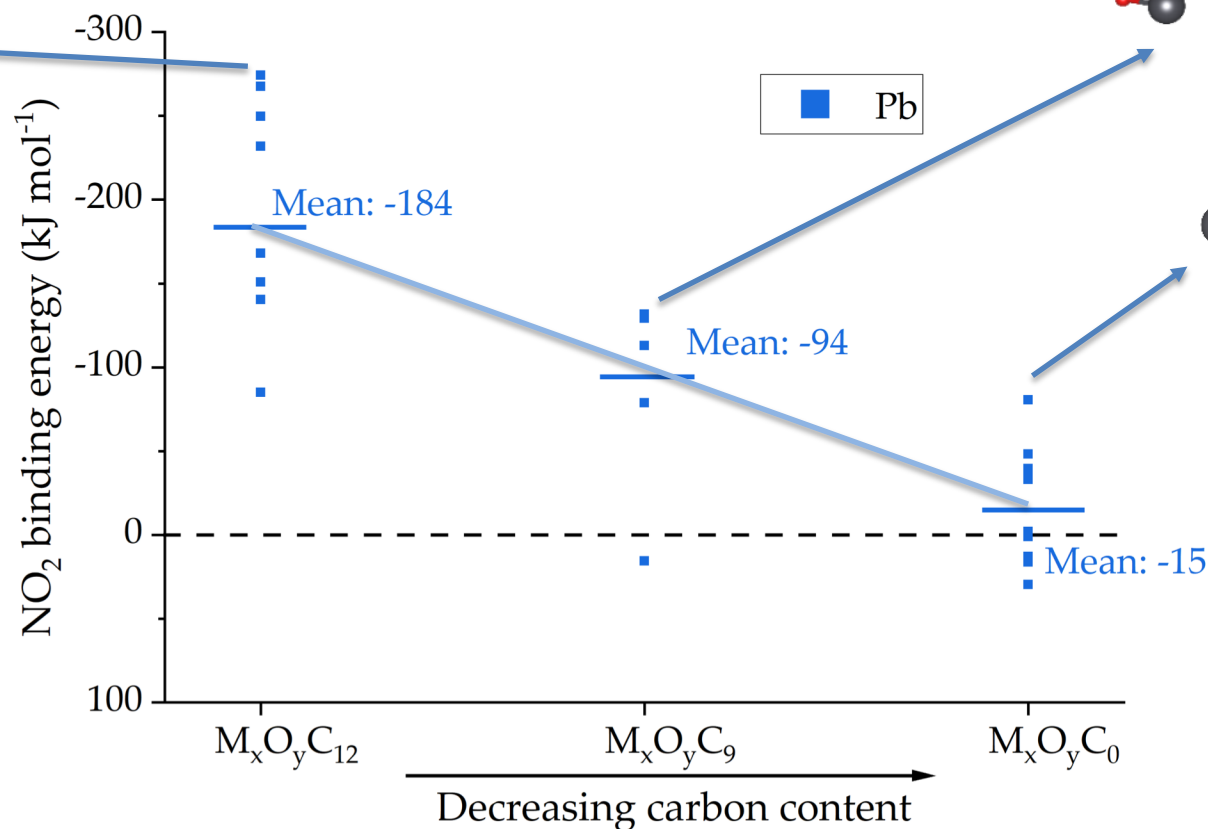


$E(\text{molecule/cluster})$

$$\text{Binding energy} = E(\text{molecule/cluster}) - E(\text{molecule}) - E(\text{cluster})$$

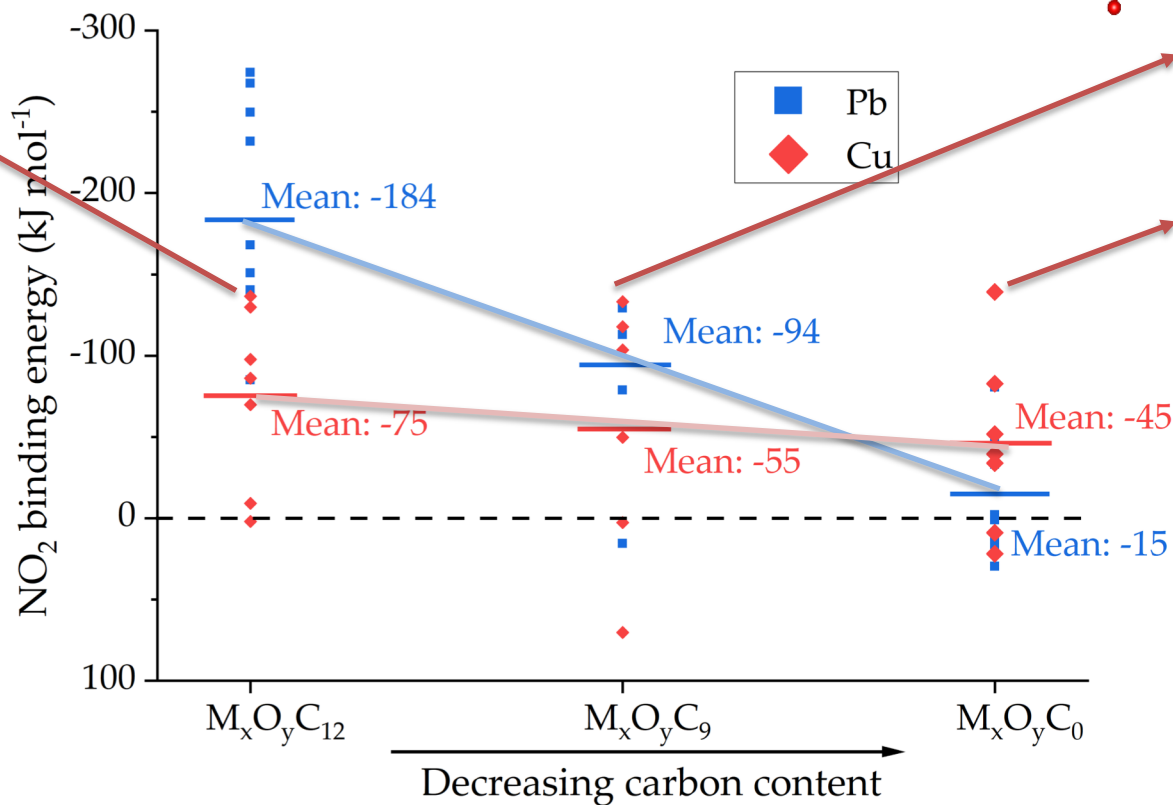
Colour scheme: red (O), dark grey (Pb), light blue (N)

# NO<sub>2</sub> binding: lead oxide



Colour scheme: red (O), dark grey (Pb), gold (C), light blue (N)

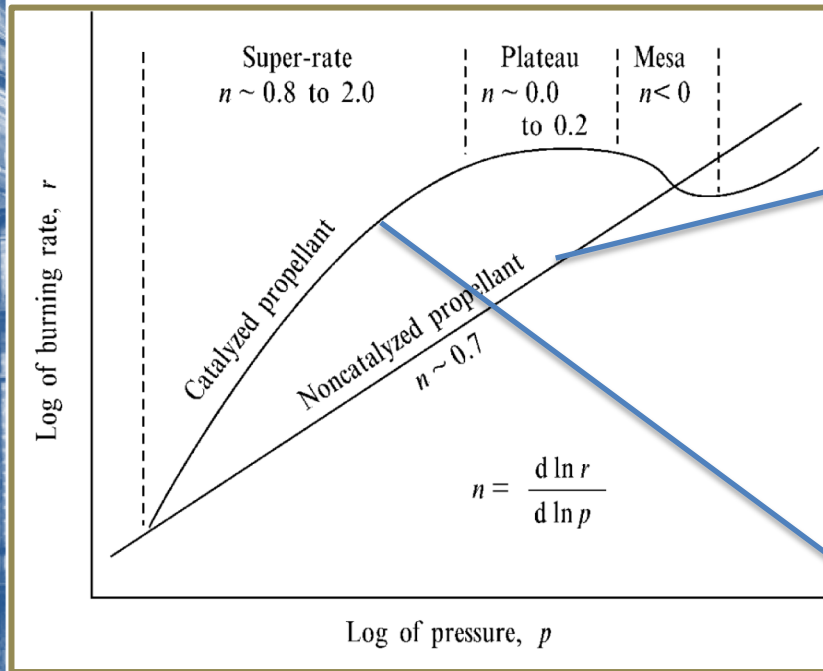
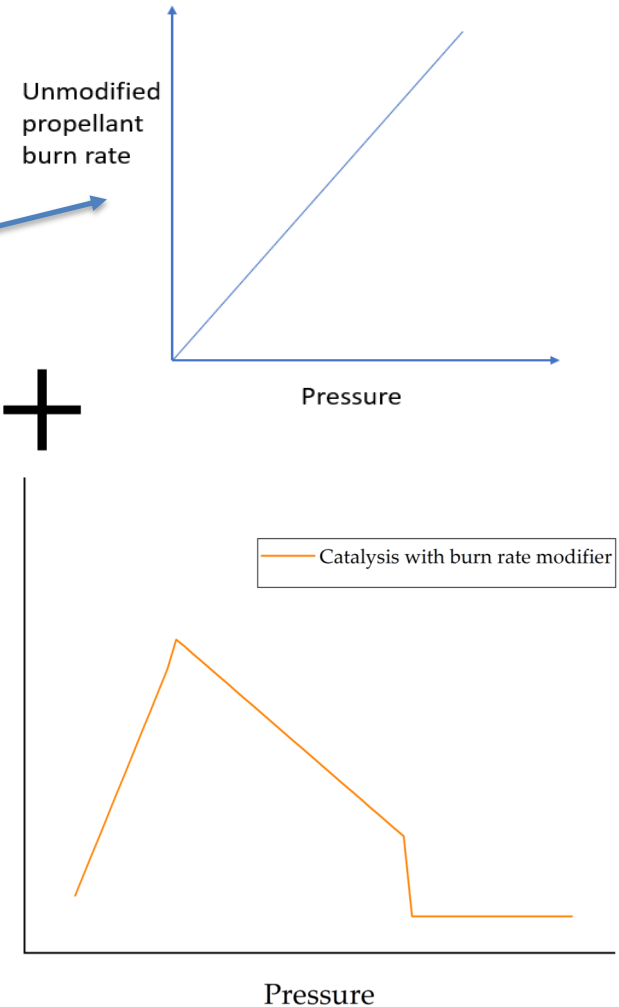
# NO<sub>2</sub> binding: copper oxide



Different gradients between Pb and Cu for NO<sub>2</sub> binding

# Burn vs pressure graphs

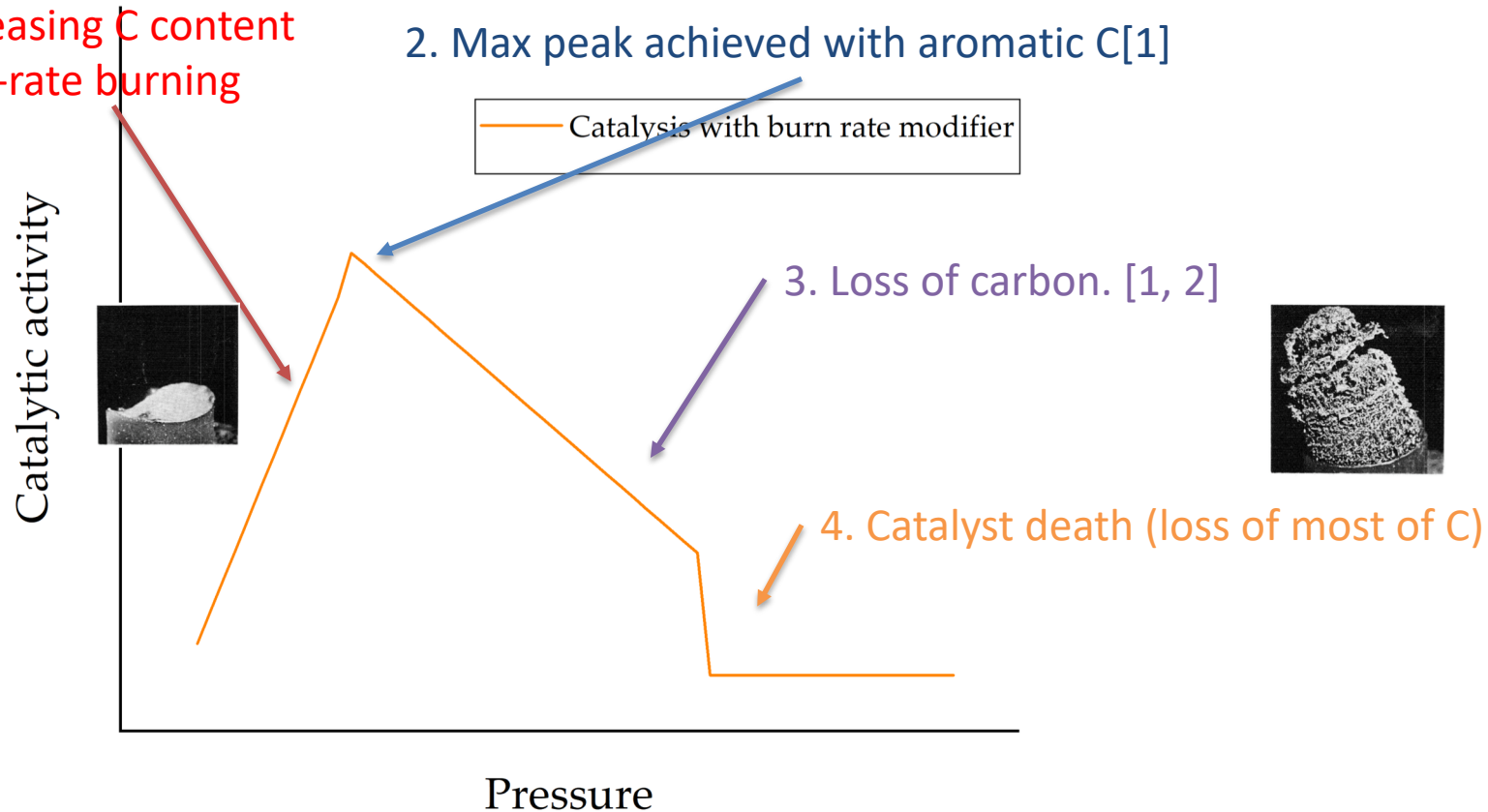
Burn rate vs pressure graph [1]



# Literature carbon soot theory: burn rate profile

1. Increasing C content  
: super-rate burning  
[1, 2]

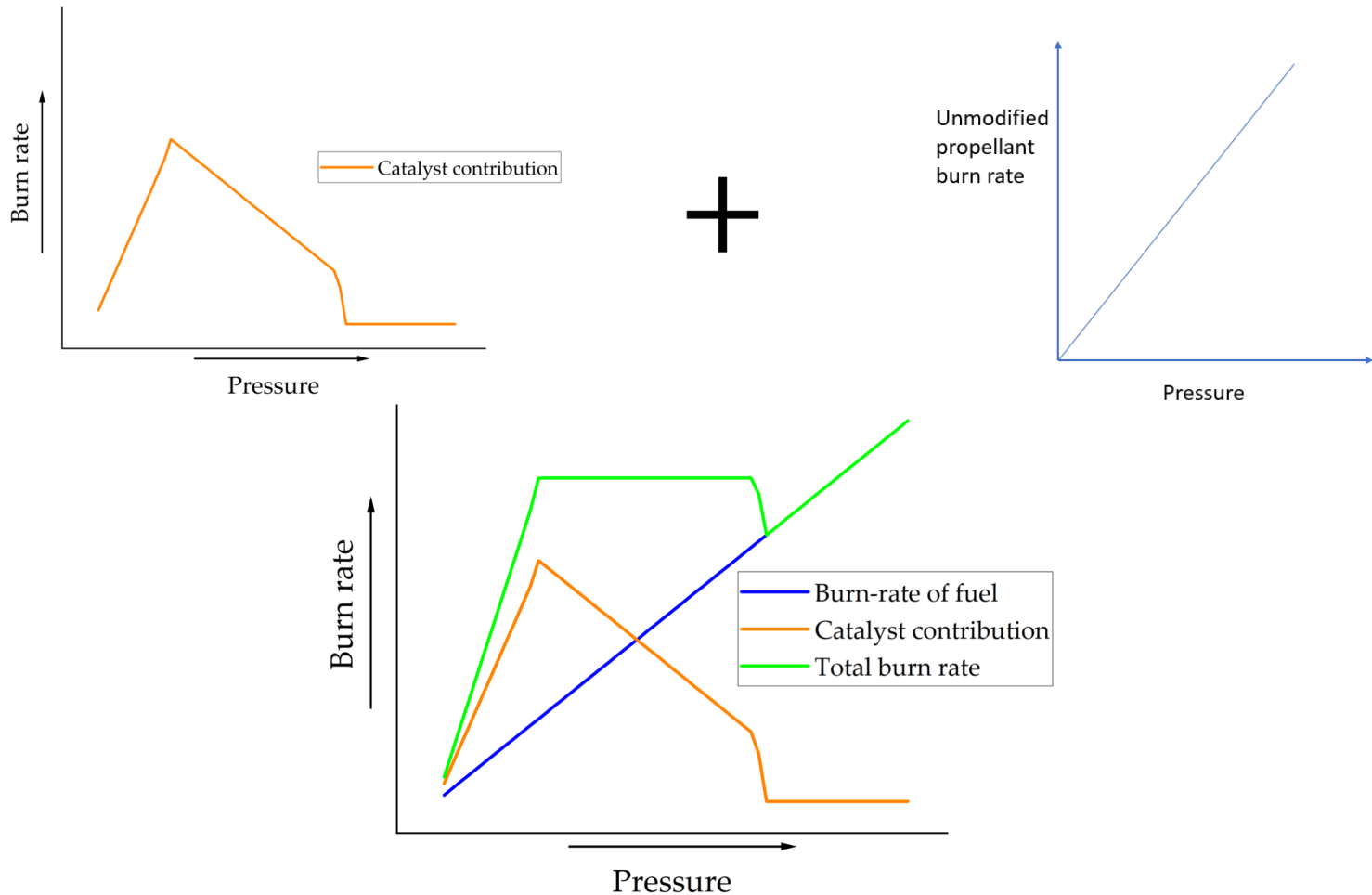
2. Max peak achieved with aromatic C[1]



[1] A. P. Denisyuk et al. *Combust. Explos. Shock Waves*, 1995, **31**, 161–167.

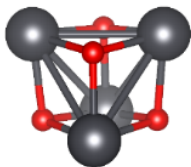
[2] D. J. Hewkin et al. *Combust. Sci. Technol.*, 1971, **2**, 307–327

# Burn vs pressure graphs

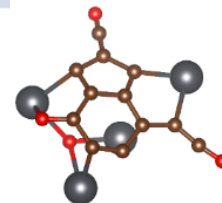


**Mesa burning**

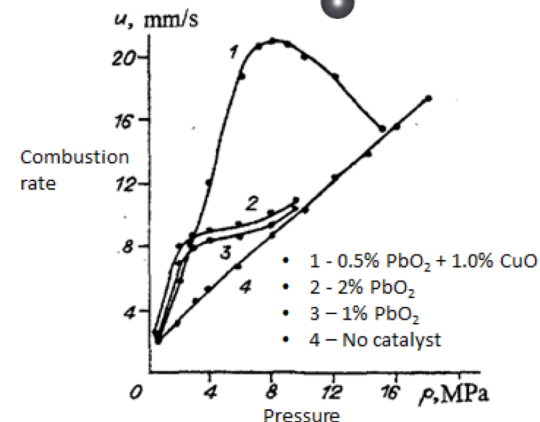
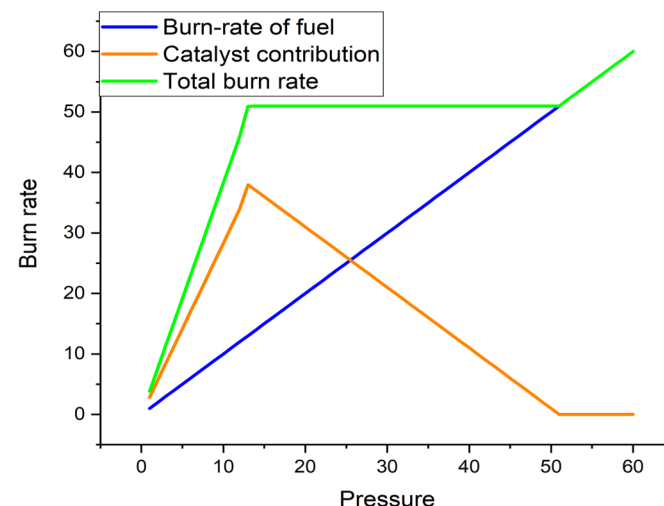
Slope catalyst  $\gg$  Slope unmodified propellant

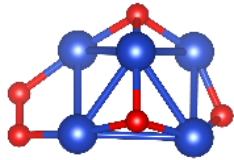


## Pb burning rate profile

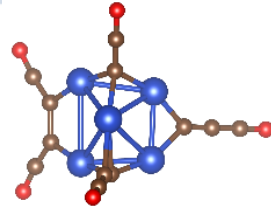


- Characteristics of lead modifiers:
  1. Super-rate burning : High levels of carbon which activate lead oxide clusters
  2. Drop in level of carbon causes plateau effect perpetuated by:
    - a) Loss of Lewis acid behaviour with loss of carbon
    - b) Weak Pb-C bonds, promotes fall off of carbon





## Pb + Cu burning rate profile

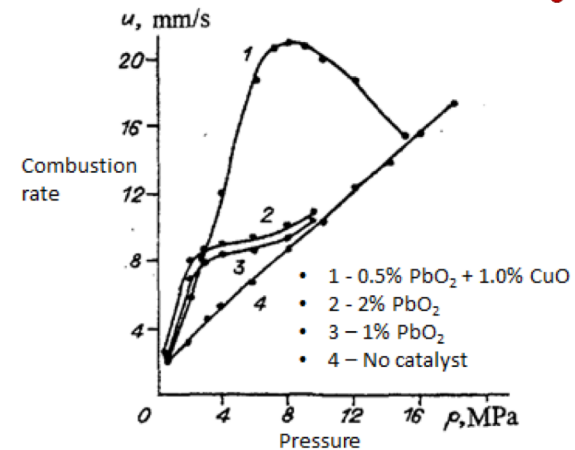
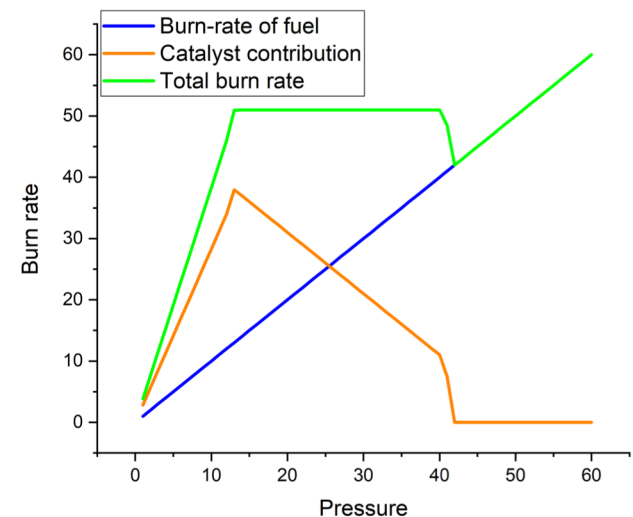


- Characteristics of lead modifiers:
- 1. Super-rate burning : High levels of carbon which activate lead oxide clusters

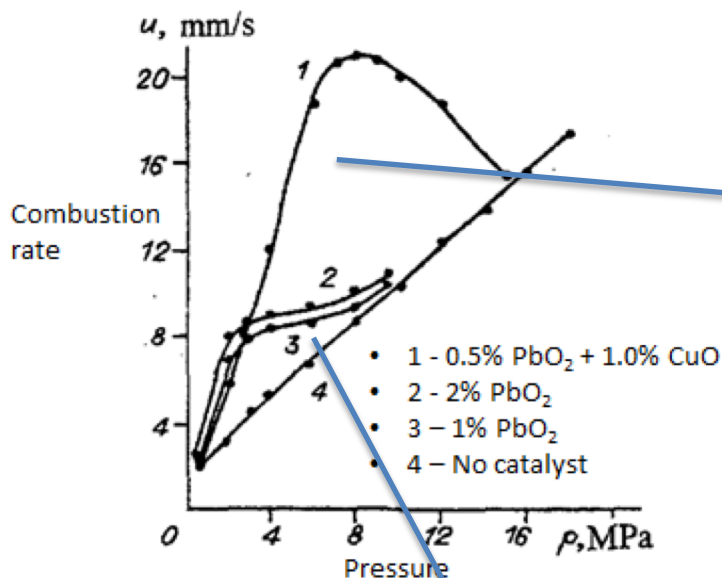
### a) Copper salts help generate carbon in combustion flame [1]

- Drop in level of carbon causes plateau effect perpetuated by:
  - Loss of Lewis acid behaviour with loss of carbon
  - Weak Pb-C bonds, promotes fall off of carbon

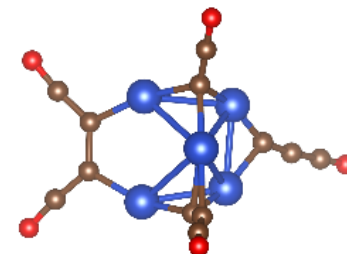
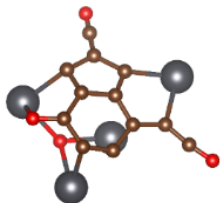
### c) In limited C, COPPER IS THERMODYNAMIC SINK FOR C PROMOTES MESA BURNING



## Conclusions : Pb vs Cu



- Copper salts help generate carbon in combustion flame [1]
- In limited carbon (high pressure) stronger Cu-C will strip carbon from Pb



- C-bound lead oxide is catalyst for small molecules
- Weak Pb-C bonds promote falls off of carbon



# Acknowledgements



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of Defence



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- Aaron Rowell
- Patrick McMaster

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