CAMBRIDGE CARES — CAMBRIDGE CENTRE FOR ADVANCED RESEARCH AND EDUCATION IN SINGAPORE LTD.

CoMo GROUP

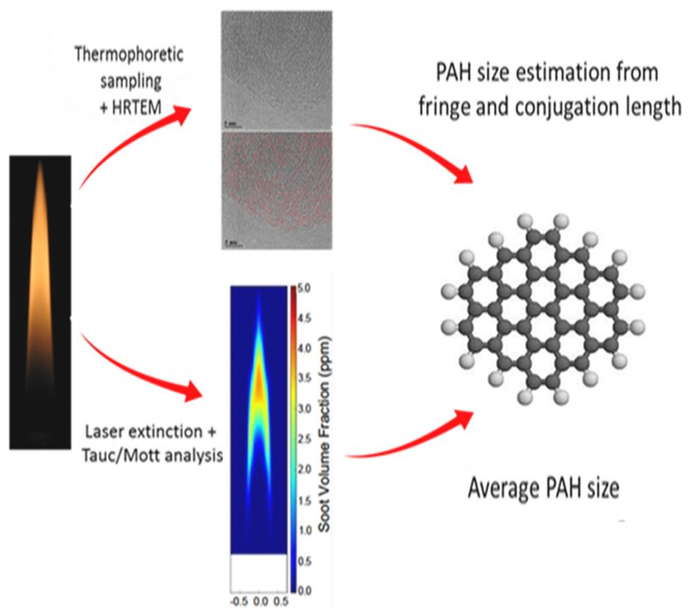
C4T

Ab initio calculation of the optical band gap of polycyclic aromatic hydrocarbons

The aim of this work is to provide density functional theory calculations of the optical band of a variety of different polycyclic aromatic hydrocarbons. This can then be compared to experimental measurements in flames to see which hydrocarbons could be present.

1. Introduction

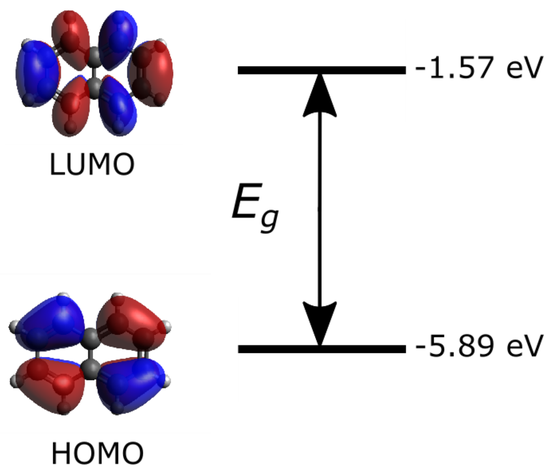
- Soot nanoparticles have adverse health impacts. They also have several applications, such as in dyes or fillers [1].
- Polycyclic aromatic hydrocarbons (PAHs) are key soot precursors, but it is not known which PAHs can form soot in a flame [2].
- Laser extinction methods can measure optical band gap (OBG) at different positions in a flame.
- The aim is to relate OBG measurements to underlying gas-phase PAH chemistry in flames.



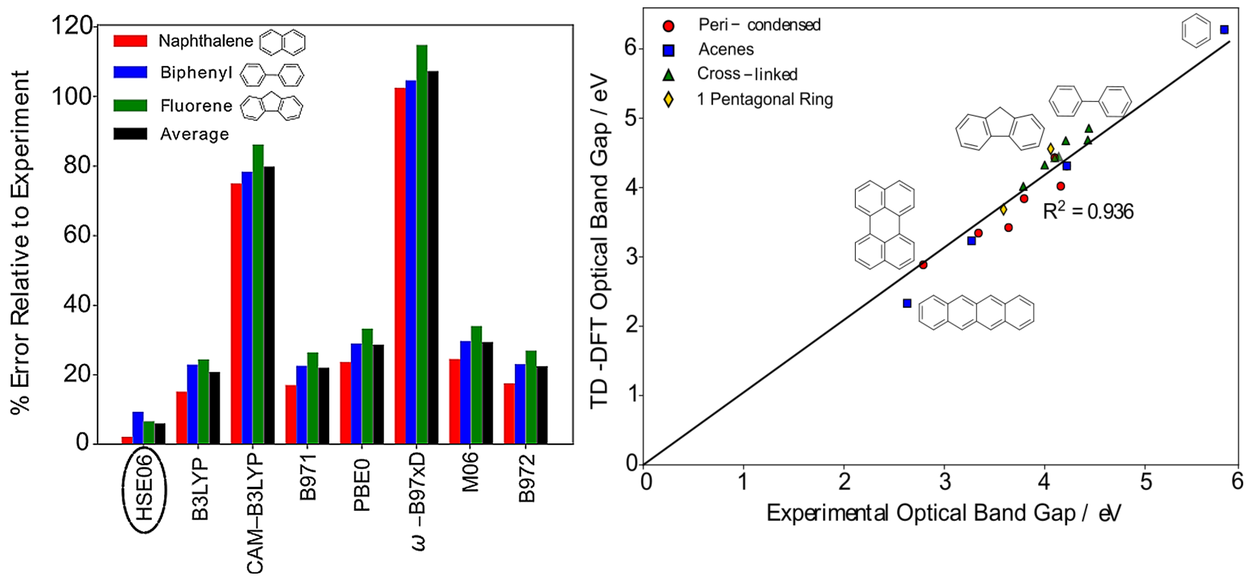
- Figure adapted from [3]

2. Methods - Density Functional Theory

- Geometry optimization and electronic structure calculations are performed using time-dependent density functional theory (TD-DFT) within GAUSSIAN09 [4].
- OBG is approximated as the difference in energy between the LUMO and HOMO:



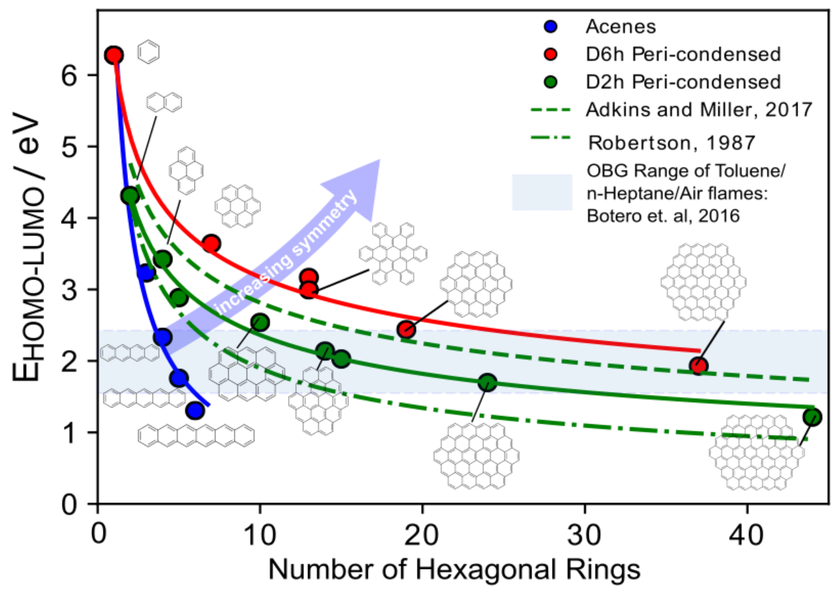
- TD-DFT calculations on the OBG of PAHs are calibrated for the first time by comparison to UV-Visible Spectroscopy measurements.
- Identify best functional using a small test set. Best functional is then tested on set of 19 PAHs.



- Further calculations are performed on larger flat PAHs that are not available commercially, and on more complex cross-linked and curved PAHs that have not been studied previously.
- Explore trends in OBG as a function of molecular properties (size, shape, curvature).
- Aim is to find PAHs with OBG in the range of 1.7 – 2.4 eV as observed in flames [3].

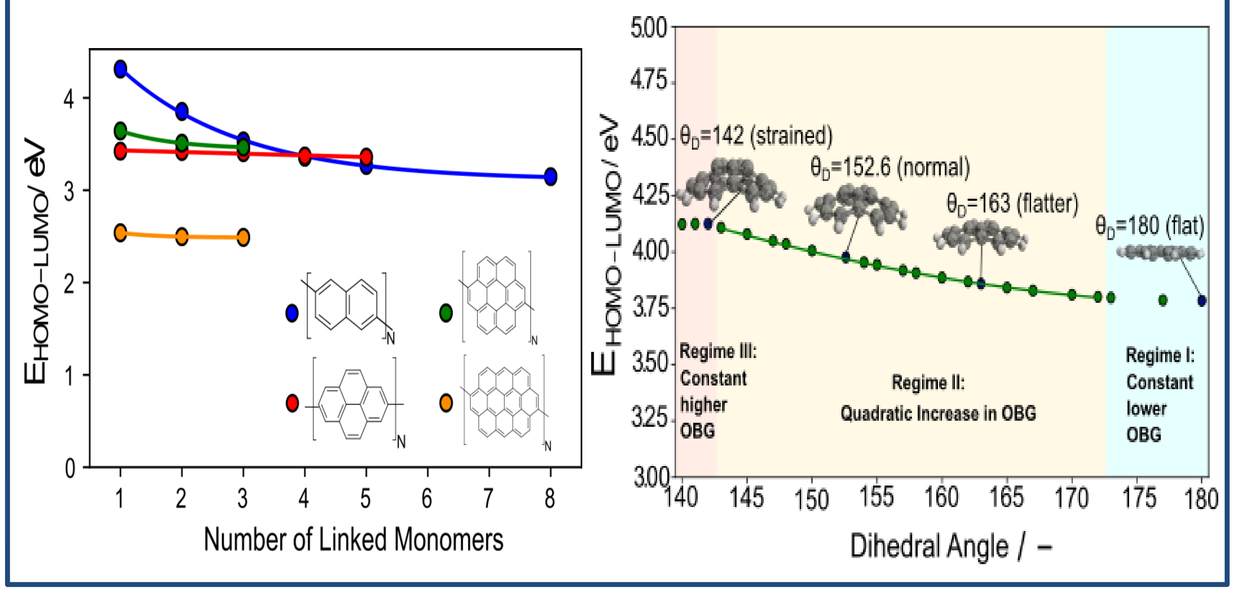
3. DFT Results

Flat PAHs



Curved and Cross-linked PAHs

- Cross-linking of PAHs minimally impacts OBG for PAHs of size pyrene and larger.
- Curved PAHs tend to have a larger OBG than flat counterparts due to σ character. The change in OBG due to curvature can be similar to a significant size difference.



4. Conclusions

- Calibration of TD-DFT calculations for determining OBG of aromatic hydrocarbons.
- The calculations suggest the following types of PAHs could account for the OBG observed in flames:
  - Moderate sized peri-condensed PAHs.
  - Cross-linked clusters of moderate peri-condensed PAHs.
  - Larger curved PAHs.
- Precisely identifying the key PAHs that govern soot formation is still not possible from analysing OBGs of more complex PAHs.

5. Further Work

- Thermodynamic and kinetic investigation of PAHs to see which could form a condensed phase at flame conditions.
- Investigate effect of oxygen-containing functional groups on the OBG of curved and cross-linked PAHs to study PAHs formed by soot oxidation.

6. References

- [1] P. Avouris, Accounts Chem. Res. 35 (2002) 1026–1034
- [2] H. Wang, M. Frenklach, Combust. Flame 110 (1997) 173 –221.
- [3] M.L. Botero, E.M. Adkins, S. Gonzalez-Calera, J.H. Miller, M. Kraft, Combust. Flame 164 (2016) 250-258.
- [4] M.J. Frisch, G.W. Trucks, H.B. Schlegel, *et al,* Gaussian09 Revision D.1, 2009, Gaussian Inc.

Acknowledgements CREATE

This project supported by the National Research Foundation, Prime Minister's Office, Singapore under its CREATE programme.

Angiras Menon, Jochen A.H. Dreyer, Jacob W. Martin, John Robertson, Markus Kraft *

Contact mk306@cam.ac.uk

CAM.CREATE C4T Cambridge Centre for Carbon Reduction in Chemical Technology