

**Berlin Institute of Technology
(TU Berlin)**

Prof. Dr. Frank Behrendt
Fakultät III: Prozesswissenschaften,
Institut für Energietechnik

Chair Energy Process Engineering and
Conversion Technologies for
Renewable Energies (EVUR)
Fasanenstr. 89
10623 Berlin

Contact
info@flame-structure-2014.com
frank.behrendt@tu-berlin.de

Berlin Institute of Technology • Fasanenstr. 89 • 10623 Berlin

George Washington University
Erin Adkins
725 21st St, NW
Washington DC 20006, USA

28. Mai 14

Confirmation of paper submission

Name: Erin Adkins
Email: webster@gwmail.gwu.edu
Co-author: Houston Miller
2nd co-author: -
3rd co-author: -
Title of Paper: Extinction Measurements for Optical Band Gap
Determination for Soot in a series of Nitrogen
Diluted Ethylene/Air Non-Premixed Flames
Program: Laminar flames
Name of Institute: George Washington University

Extinction Measurements for Optical Band Gap Determination for Soot in a series of Nitrogen Diluted Ethylene/Air Non-Premixed Flames

Erin M. Adkins¹ and J. Houston Miller¹

¹George Washington University 725 21st St, NW Room 107 Washington, DC 20052

Abstract

A SuperContinuum light source was used to measure extinction in a full range of nitrogen diluted, ethylene/air, non premixed flames in order to gain information about the size in the soot formation mechanism that PAH molecular growth transitions to physical agglomeration. Using Tauc/Davis-Mott analysis, the optical band gap (OBG) was determined from the extinction profiles. A previously published relationship between the calculated HOMO-LUMO gaps of a variety of D_{2h} PAH molecules and molecular size, allowed for the size of PAH throughout the flame to be mapped based on the experimentally determined OBG. These results suggest PAH condensation beginning with species about the size of circumpyrene.

Introduction

In the soot formation mechanism published by Frenklach and Wang [1], initial chemistry forms unsaturated hydrocarbon radicals that undergo cyclization to form benzene. Continued growth is modeled as a combination of chemical growth through successive acetylene addition and physical coagulation of PAH [2]. They found that particle size was determined primarily by the latter and that the size of PAHs did not vary throughout the particle inception zone. This poses the important question: at what size do the PAH become large enough that intermolecular forces become large enough that chemical bonding is no longer a requirement for particle growth?

This issue has sparked considerable debate in the combustion community with some models invoking coagulation for species as small as pyrene and others suggesting coagulation of only much larger PAH. However there is limited experimental evidence that defines a molecular size where this transition occurs [3-5]. In both the work presented here and recent publications from our lab, we have applied Raman spectroscopy and Tauc analysis of visible light extinction measurements to define the transition and have found that it occurs at modest molecular size [4, 5].

In the late 1960's and early 1970's, Tauc and Davis/Mott demonstrated that the low energy (long wavelength) edge of the optical absorption of amorphous semiconductors provides a probe of localized states [6-9]. Therefore the optical band gap (OBG), the energy difference between occupied and unoccupied π orbitals, can be calculated from **Equation 1**.

Equation 1.

$$hv \cdot \alpha \approx (hv - E_g^{opt})^r$$

Where α is the extinction coefficient, E_g^{opt} is the OBG, and r is a constant that changes based on whether the observed optical transition is quantum mechanically allowed and if the optical transition is direct or indirect [6-9]. For our analysis, a value of 0.5 is used for r corresponding to a direct allowed transition [9].

The Tauc/Davis-Mott model allows for the OBG to be experimentally determined from an extinction measurement. However, it is necessary to correlate the observed OBG to molecular size in order to gain insight to the size of aromatics throughout the flame. Building on Robertson's early theoretical work on the electronic structure of amorphous carbon [10, 11], Robertson and Ferrari showed that systems with sp^2 character, such as soot, have electronic properties that are dominated by π - π^* interactions. They then showed that the OBG scales inversely with the number of aromatic rings in an aggregate (**Equation 2**).

Equation 2.

$$E_g \approx \frac{2\gamma}{M^{\frac{1}{2}}} \approx 2\gamma \left(\frac{a}{L_a} \right)$$

Where γ is a measure of π - π interaction, M is the number of aromatic rings in a cluster, a is the lattice spacing, and L_a is the conjugation length [12-14]. This relationship needs to be further quantified before an experimentally determined OBG can be correlated to a molecular size.

In the initial Tauc experiment publication by our group [4], it was postulated that if nascent soot particle morphology is dominated by clusters of moderately sized PAH structures, then there will be a

correlation between measured OBGs and the “band gap” of the molecular structure, defined by the energy difference between the highest occupied and lowest unoccupied molecular orbitals of individual PAH. A GAMESS-US computational chemistry package was used to perform time-dependent, density functional theory calculations in order to calculate the electronic structure for several D_{2h} – symmetrized PAH species, using optimized molecular geometries obtained from the *Theoretical Spectral Database Of Polycyclic Aromatic Hydrocarbons* [15]. The species studied represented a size and morphology range where growth occurs through only chemical mechanisms (for low masses) to a size regime where physical agglomeration is possible (defining a range of 200-800 Da). By fitting the computational results to the relationship proposed by Robertson and Ferrari [12-14], the following relationship (**Equation 3**) was generated, which correlates experimentally determined band gaps to the size of the PAH in the aggregate.

$$E_g^{opt} = \frac{5.8076}{M^{1/2}} + 0.5413$$

Equation 3.

In the current work, we are revisiting the extinction measurements utilizing Tauc/Davis-Mott analysis in a C_2H_4/N_2 flame system with four levels of dilution with a SuperContinuum light source. The introduction of a source with higher spectral range, substantially higher power, and spatial coherence adds more fidelity to the prior measurements. The coupling of this new light source with analysis throughout the complete set of flames and throughout the entire range of heights allows for a more robust analysis of OBG.

Approach

Figure 1 shows the extinction schematic where light from a SuperContinuum light source (NKT Photonics EXB-4) is collimated, expanded, and directed into a monochromator. The dispersed light is split into a power metering channel and a channel that is periscoped and focused into the flame. The transmitted light is then recollimated before the detector. The burner is mounted on a motorized translational stage (Velmex BiSlide X15-Z10) that moves the burner both horizontally and vertically.

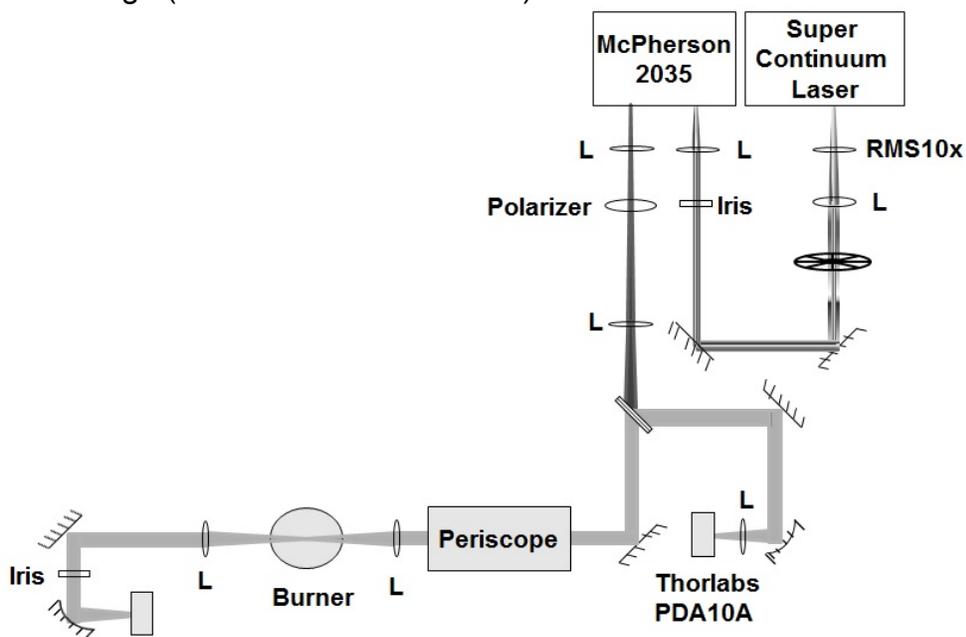


Figure 1. Line of Sight Extinction Schematic

Results and Discussion

Because the studied flame is axi-symmetric, the raw line of sight extinction will be a combination of contributions from the different radial positions the radiation passes through, making it necessary to perform a tomographic reconstruction of the radial extinction field prior to Tauc/Davis-Mott analysis. In this analysis the straight line portion of a plot of $(h\nu)^{1/r}$ as a function of $h\nu$ is extrapolated to the x-intercept, which is equal to the OBG. This analysis procedure was repeated at all flame positions where there was substantial soot concentrations in each of the flames studied.

Figure 2 depicts the experimentally determined OBG including propagated error at 2.0cm above the burner in the 60%-C₂H₄/40%-N₂ flame compared to the computed soot volume fraction from the Smooke group at Yale [16]. There is a clear evolution in the OBG as a function of radial position where the OBG is lowest in the region where the soot volume fraction is the highest. This same trend is observed with height above the burner. Using the relationship proposed by Robertson and Ferrari (**Equation 2**), this means that PAHs making up the soot particles tend to be larger in the areas where the soot volume fraction is larger.

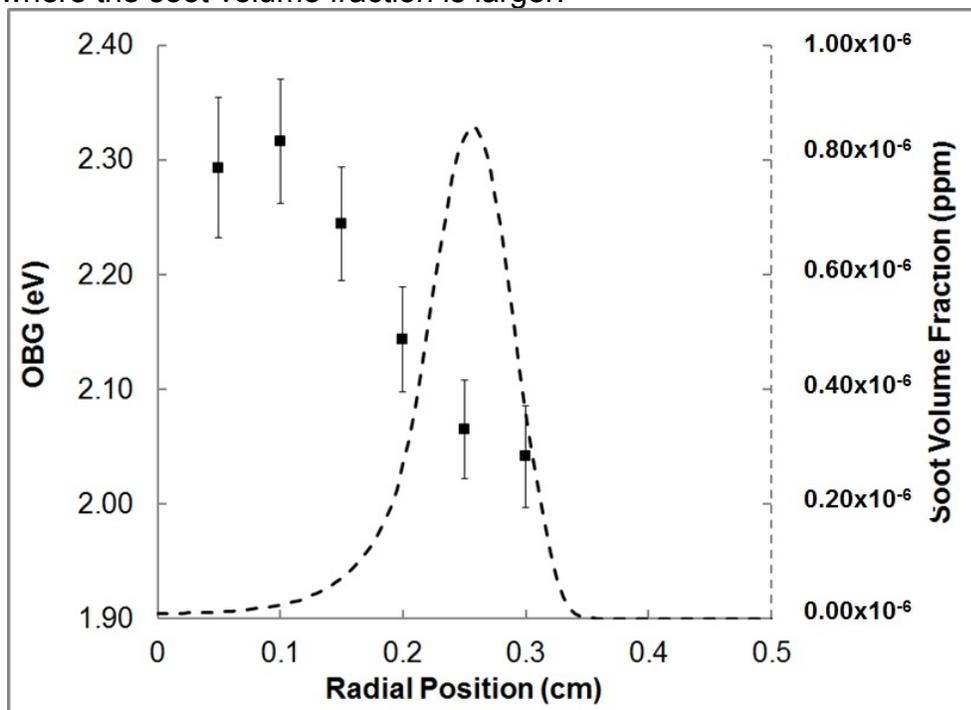


Figure 2. Experimentally determined OBG (squares) as a function of radial position at 2.0cm above the burner (60%-Ethylene/40%-Nitrogen). The **dashed** line depicts the soot volume fraction calculated by the Smooke Group at Yale at the same flame position.

Conclusions

Figure 3 combines the relationship between the number of aromatic rings and the OBG (**Equation 3**) and the relationship between the number of aromatic rings and the conjugation length to relate the experimentally determined OBG to the physical size of the PAH it belongs to. The grey diagonals represent how the range of experimentally determined OBG throughout the flame manifest in the conversion from OBG to number of aromatic rings and number of aromatic rings to conjugation length. An evolution in OBG was observed throughout all flame systems with a consistent range of OBG observed between approximately 1.9eV and 2.3eV. **Figure 3** shows that this variation correlates to PAHs between 10-20 aromatic rings making up soot particles in the flame. This would indicate that throughout the flame soot particles are made up of PAHs between the size of ovalene and circumcoronene. Averaging over all positions the average OBG was approximately 2.09eV for all flame systems. The observed optical band gap is consistent with a PAH of about 14 rings or a conjugation length of 0.96nm. These results suggest that PAH condensation beginning with species about the size of circumpyrene.

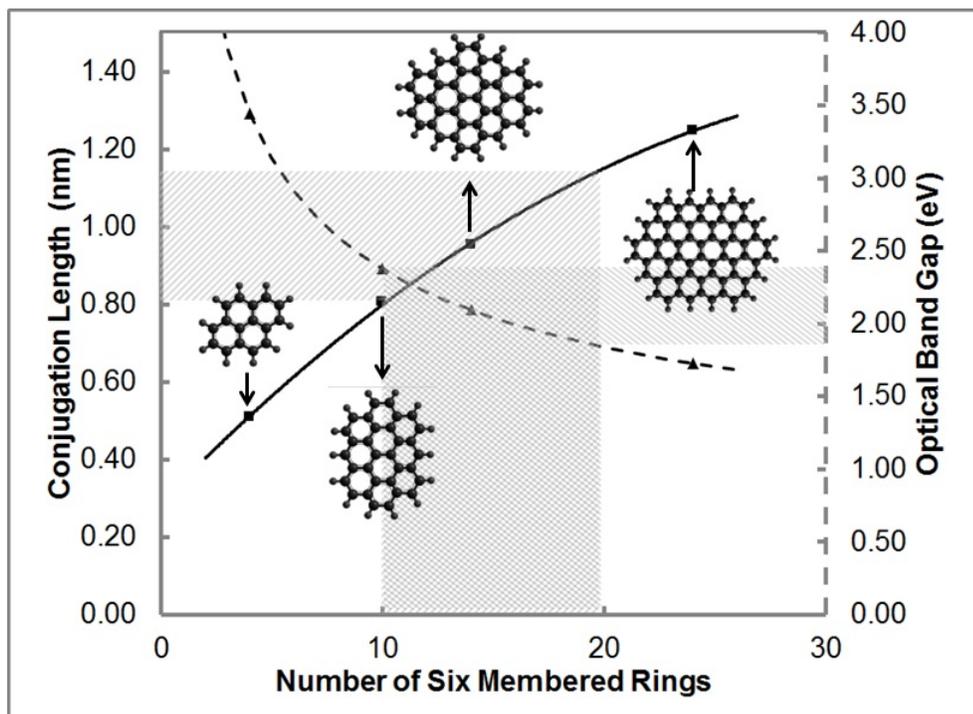


Figure 3. Comparison between calculated HOMO-LUMO energy gaps (OBG) with number of aromatic rings and conjugation length. The dashed line and triangles show the relationship between OBG and number of rings. The solid line and squares show the relationship between conjugation length and number of rings. The grey diagonal lines depict how the range of OBG observed throughout the flame correlate to physical morphology parameters in the 60%-Ethylene/40% Nitrogen flame.

Acknowledgements

This material is based upon work supported by the U.S. National Science Foundation under grant number CBET-0828950 and CBET-1142284 with Drs. Philip Westmoreland, Avind Atreya, and Ruy-Hung Chen serving as technical monitors. We would like to thank our colleagues, Marshall Long and Mitchell Smooke and their research groups, at Yale University for a continuous, productive collaboration.

References

1. M. Frenklach and H. Wang, Symposium (International) on Combustion, [Proceedings] 23rd (1991) 1559-1566.
2. M. Frenklach and H. Wang, Proceedings of the Combustion Institute 23 (1998) 1559-1566.
3. J. Happold, et al., Rapid Communications in Mass Spectrometry 21 (7) (2007) 1247-1254.
4. J. H. Miller, et al., Proceedings of the Combustion Institute 34 (2) (2013) 3669-3675.
5. J. D. Herdman, et al., Carbon 49 (15) (2011) 5298-5311.
6. J. Tauc, et al., physica status solidi (b) 15 (2) (1966) 627-637.
7. D. L. Wood and J. Tauc, Physical Review B: Solid State [3]5 (8) (1972) 3144-3151.
8. E. Davis and N. Mott, Philosophical Magazine 22 (179) (1970) 0903-0922.
9. E. A. Davis and N. F. Mott, Electronic Processes in Non-Crystalline Materials, Oxford University Press, Oxford, Oxford University Press, 2012, p. Non-Crystalline SemiConductors - Optical Absorption.
10. J. Robertson and E. P. O'Reilly, Physical Review B: Condensed Matter and Materials Physics 35 (6) (1987) 2946-2957.
11. J. Robertson, World of Carbon 1 (Graphite and Precursors) (2001) 249-273.
12. L. G. Cancado, et al., Applied Physics Letters 88 (2006) 163106-163106-163106-163103.
13. A. C. Ferrari and J. Robertson, Physical Review B: Condensed Matter and Materials Physics 61 (20) (2000) 14095-14107.
14. A. C. Ferrari and J. Robertson, Physical Review B 64 (2001) 075414-075411-075414-075413.
15. G. Mallocci, available at <<http://astrochemistry.ca.astro.it/database/pahs.html>>.
16. M. D. Smooke, et al., Combustion and Flame 143 (4) (2005) 613-628.