Extinction Measurements for Determination of Optical Band Gaps for Soot in Nitrogen-diluted, Ethylene/Air Non-premixed Flames

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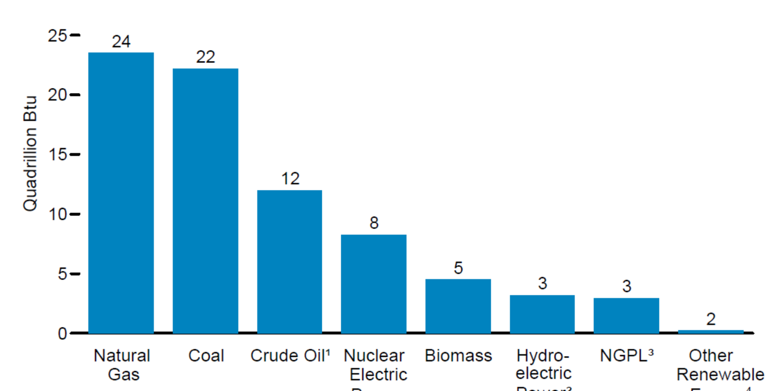
Abstract

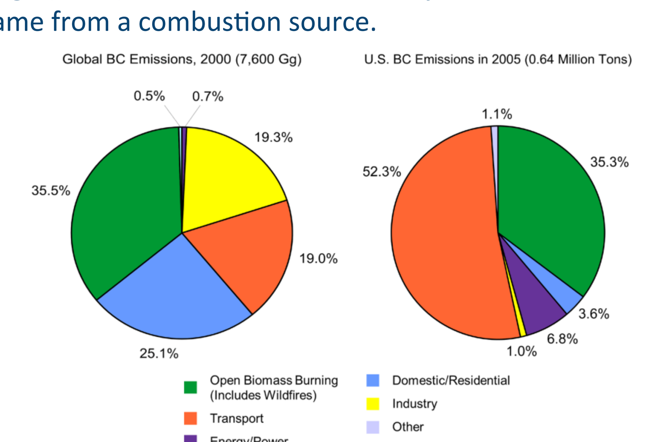
Visible light extinction was measured at the full range of heights in a nitrogen-diluted, ethylene/air, non-premixed flame and this data was used to determine the optical band gap, E_g^{opt}, as a function of radial position. This work builds on recent Raman and optical band gap studies in our lab, which provided experimental support to the model of soot formation where the transition from chemical to physical growth starts with species with molecular masses of only several hundred Daltons. In the current study, light from a SuperContinuum light source 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. After tomographic reconstruction of the radial extinction field, the optical band gap was derived from the near edge absorption feature using Tauc analysis. This approach was repeated at heights from 1.0 to 4.5 cm above the burner, showing evolution in the optical band gap throughout the flame. Observed optical band gaps span the range from 1.96eV to 2.37 eV, where lower band gaps are observed in regions of the flame with the largest soot concentration. Comparing these results to previously published computational results from our lab relating calculated HOMO-LUMO gaps for a variety of D_{2h} PAH molecules to the number of aromatic rings in the structure, showed that the observed optical band gaps are consistent with PAHs between 10 and 17 rings in size or a conjugation length between 0.8 and 1.0 nm. This result agrees with the lower edge of the PAH sizes reported in our recent Raman work that suggest 1.0 – 1.2 nm conjugation lengths. These results are consistent with PAH condensation beginning with species about the size of circumpyrene.

Why Study Combustion?



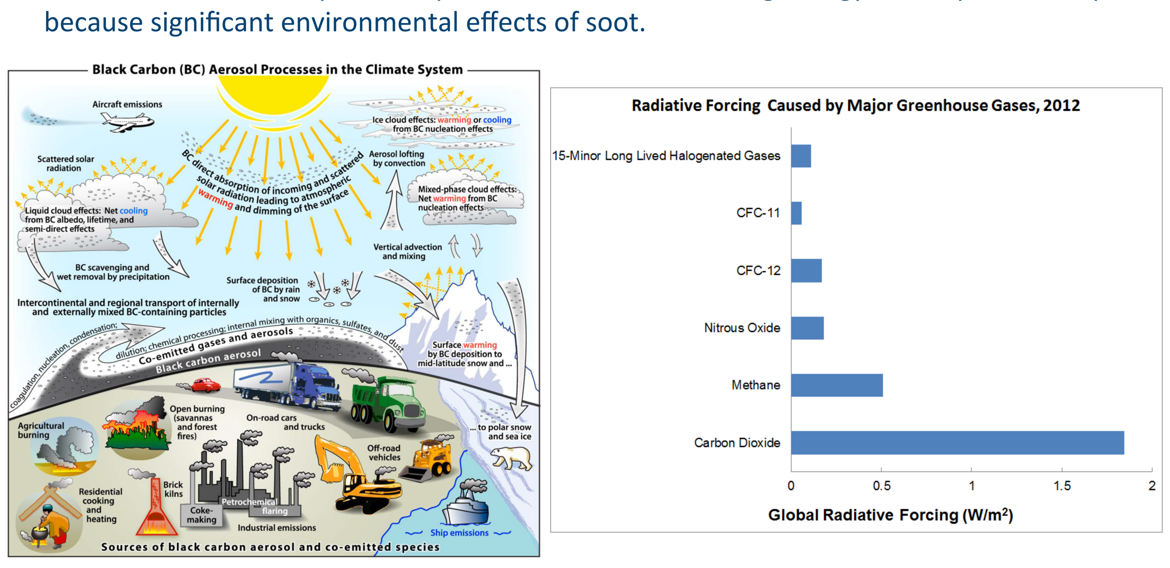
U.S. Energy Information Administration: Annual Energy Review (2011).

- Between natural gas, coal, crude oil, and biomass just under 80% of energy consumed in the US in 2011 came from a combustion source.



EPA Report to Congress on Black Carbon (2010).

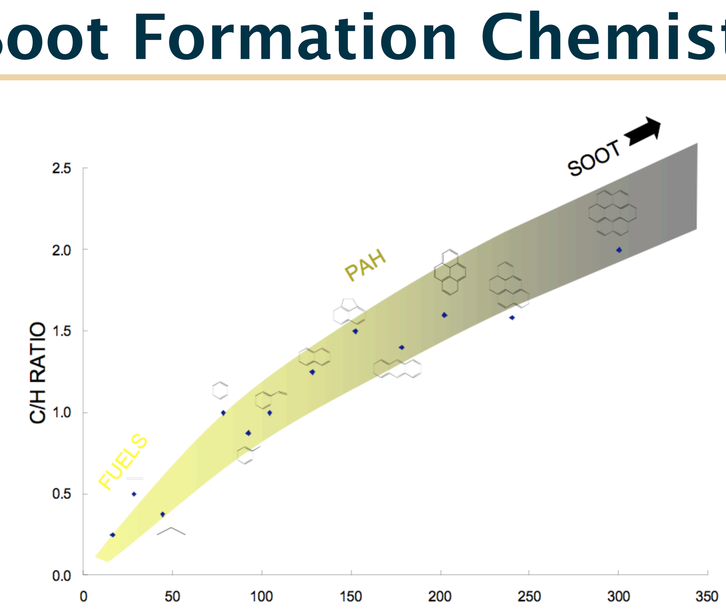
- The US contributes about 8% of the global emissions of black carbon or soot. Because combustion is not likely to be superseded soon in its leading energy role, a problem is posed because significant environmental effects of soot.



The NOAA Annual Greenhouse Gas Index (2013). Journal of Geophysical Research: Atmospheres 118 5380-5552 (2013).

- Soot's impact on climate is complicated because soot has both warming and cooling forces depending on it's location in the environment. These effects were recently quantified to estimated the radiative forcing caused by black carbon.
- This study published a total climate forcing of 1.1W/m², making it the second most important anthropogenic emission in terms of climate forcing in the atmosphere, below CO_2 and above CH_4.
- Anthropogenic contributions are equal to about 1% total energy budget speaks to the growing problem of climate change.
- In the next 20 to 30 years anthropogenic contributions are expected to cause about 2 rise in global temperature. Because soot has a significantly shorter atmospheric lifetime than CO_2 and CH_4, adding it to climate change mitigation strategies may have more of an effect over the next few decades than only considering greenhouse gases.
- **In order to most effectively mitigate the negative effects of combustion processes the chemical and physical processes need to be well understood.**

Soot Formation Chemistry



- Initially, unsaturated hydrocarbon radicals are formed from the fuel and then undergo cyclization to form benzene.
- Polyaromatic hydrocarbons (PAH) are then formed through a hydrogen abstraction reaction followed by acetylene addition.
- At some point the magnitude of the non-bonding interactions becomes large enough that chemical bonding is no longer a requirement for sticking. The size of molecule where this transition occurs is highly contested in the combustion community.

Tauc Analysis

In 2000, Robertson and Ferrari showed the correlation between correlation length, L_a; the number of aromatic rings, M; and the optical band gap, E_g.

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

Physical Review B 61 14095-14107(2000).

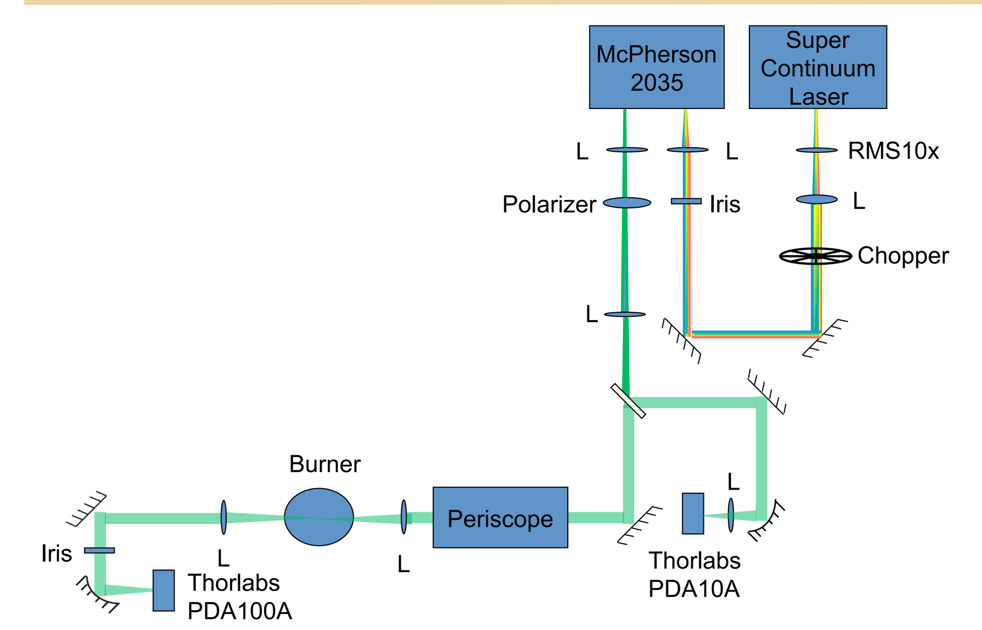
In the early 1970's, Tauc showed that the optical band gap energy can be measured from the absorption constant from the edge of a strong absorption feature.

$$h\nu \bullet \alpha \approx \left(h\nu - E_g^{opt}\right)^r$$

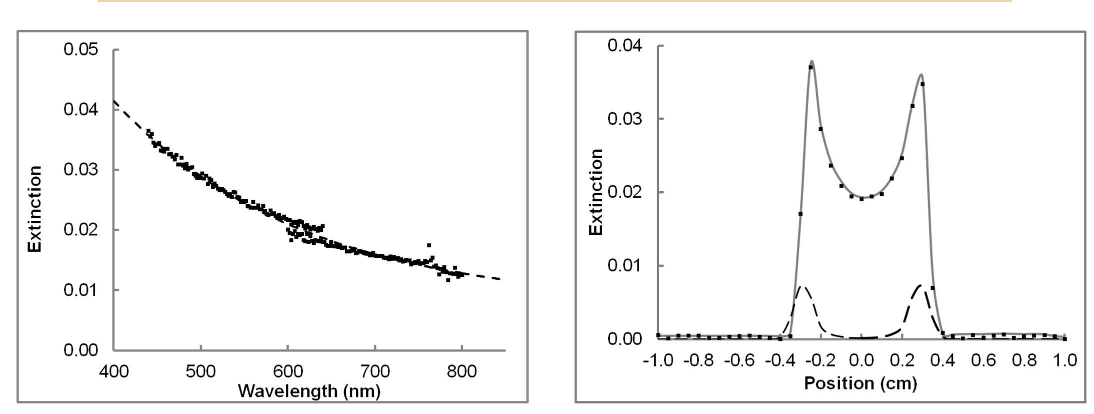
Physical Review B 5 3144-3151(1972).

Tauc analysis is conducted by plotting $(h\nu*\alpha)^{1/r}$ as a function of hv and then fitting the linear portion with a line of best fit. The x-intercept of this fit is equal to the optical band gap (OBG). Applying the combination of Tauc analysis and the relationship reported by Robertson and Ferrari, it is possible to relate the OBG to the size of the PAH making up soot particles.

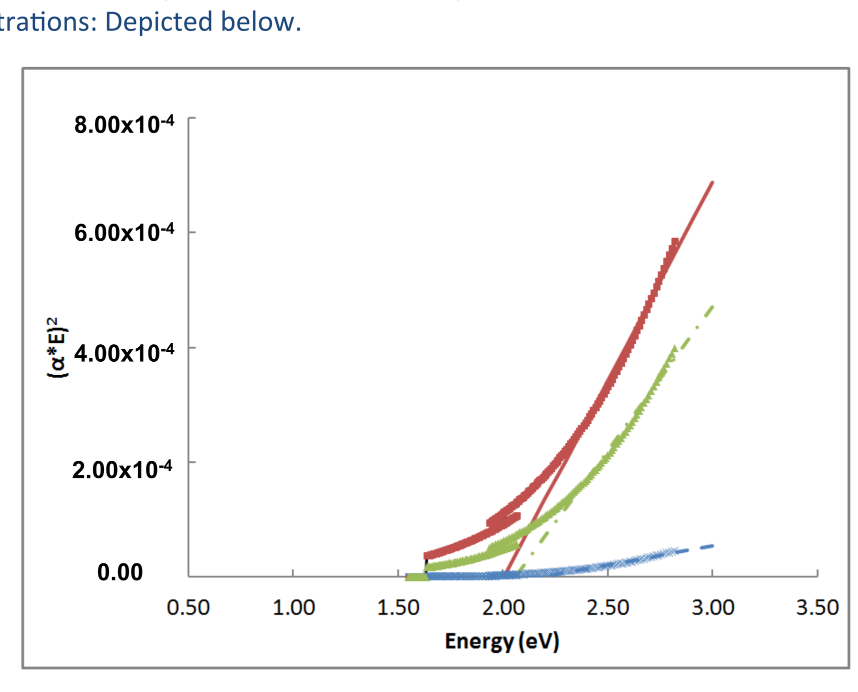
Extinction Schematic for Tauc Analysis



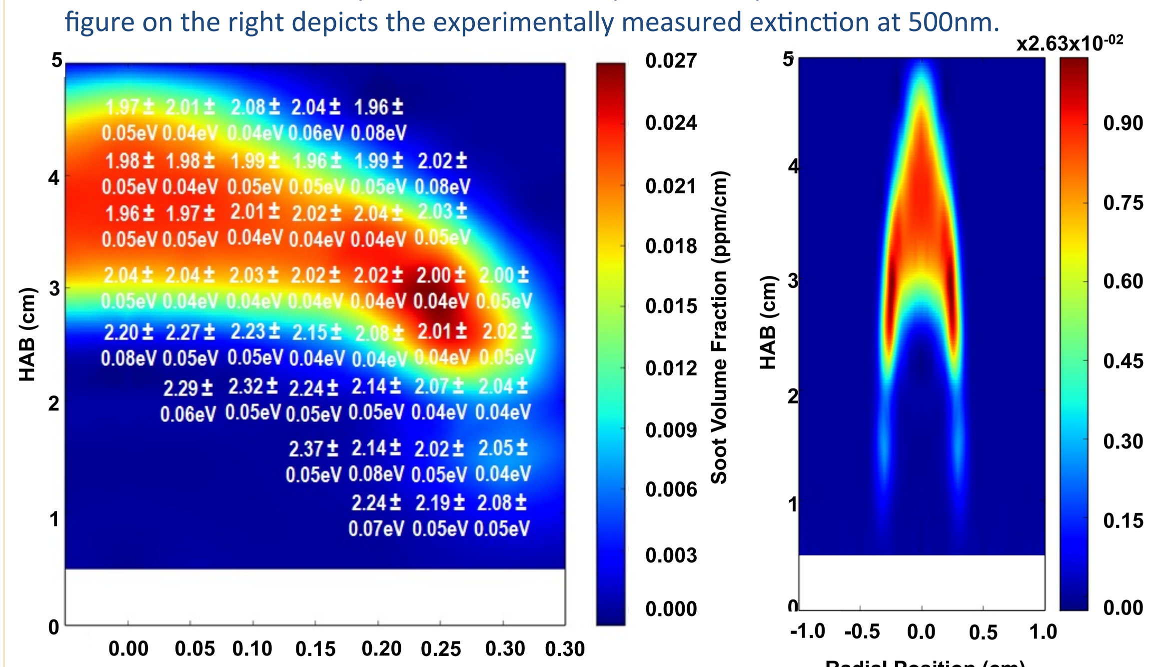
Extinction Measurements Analysis and Results



- Collect line-of-sight extinction data: The squares in both figures depict the line-of-sight extinction data collected 2cm above the burner 0.20cm from the centerline of the 60%Ethylene/40%Nitrogen flame.
- Fit wavelength spectra with exponential fit to mitigate noise: The dashed line in the figure on the left depicts this fit.
- Use 3pt Dasch Matrix Abel Inversion at each wavelength to extract the radial extinction profile: The dashed line in right hand figure shows the resulting profile from this approach.
- Conduct Tauc analysis over the radial positions where there is substantial soot concentrations: Depicted below.



- Repeat analysis at each HAB: The figure on the left below depicts the soot volume fraction as a function of flame position with the experimentally determined OBG overlaid. The figure on the right depicts the experimentally measured extinction at 500nm.



Acknowledgements

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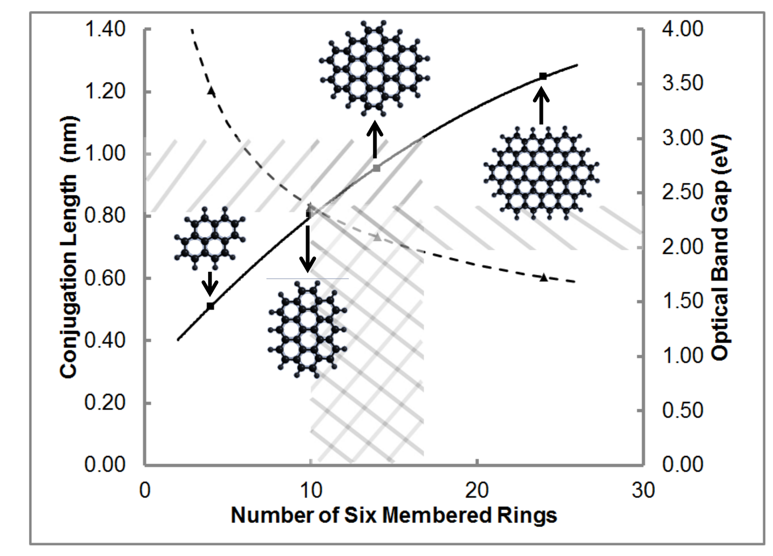
Comparison between Experiment and Computations



HOMO-LUMO energy gaps (OBG) spanning a range of PAH sizes were calculated to provide a correlation between the molecular size and OBG. The dashed line and triangles show the computed relationship between OBG and number of rings. The solid line and squares show the geometric 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.

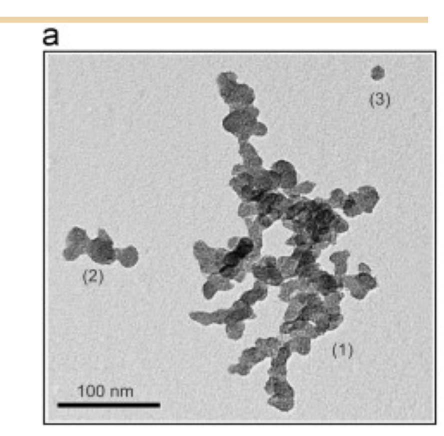
Next Steps - Fractal Aggregate Scattering Measurements

- Fractal Aggregates are scale invariant and thus statistically the same regardless of scale.

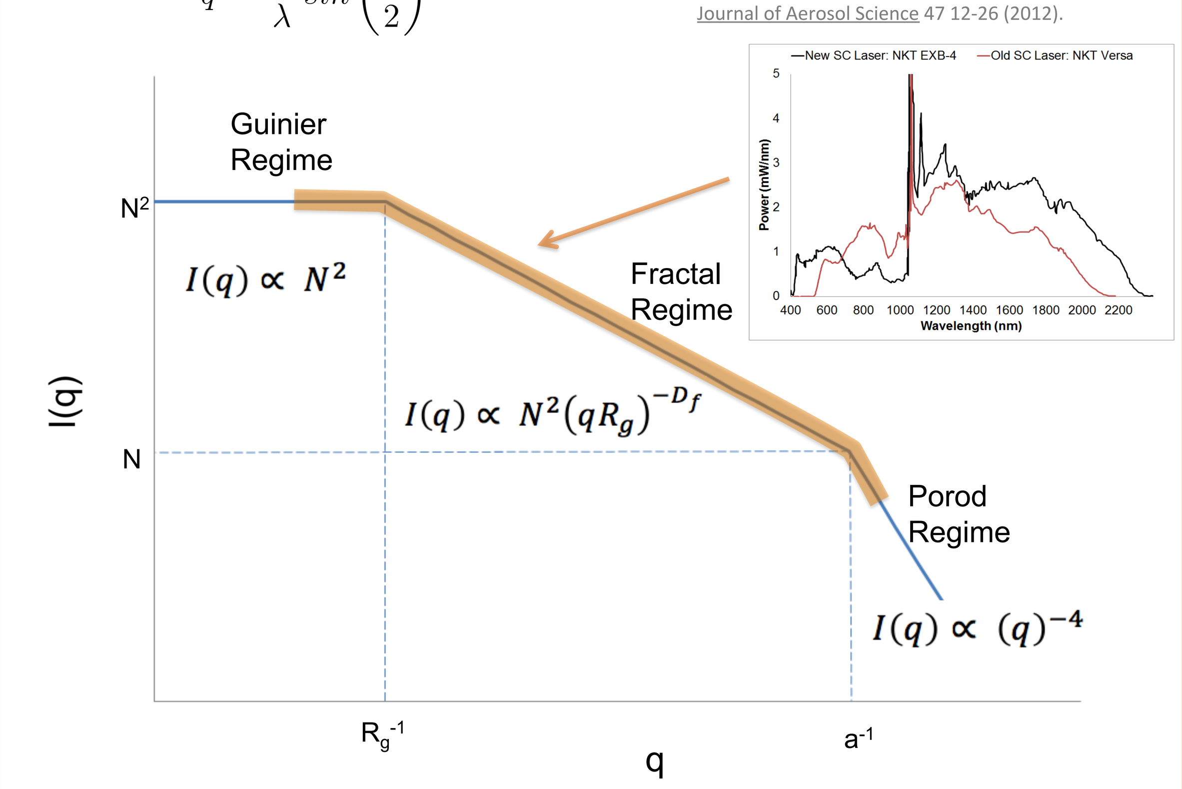
$$N = k_0\left(\frac{R_g}{a}\right)^{D_f}$$

- Rayleigh-Debye-Gans Scattering Theory can be used to derive structural insight.

$$q = \frac{4\pi}{\lambda} sin\left(\frac{\theta}{2}\right)$$

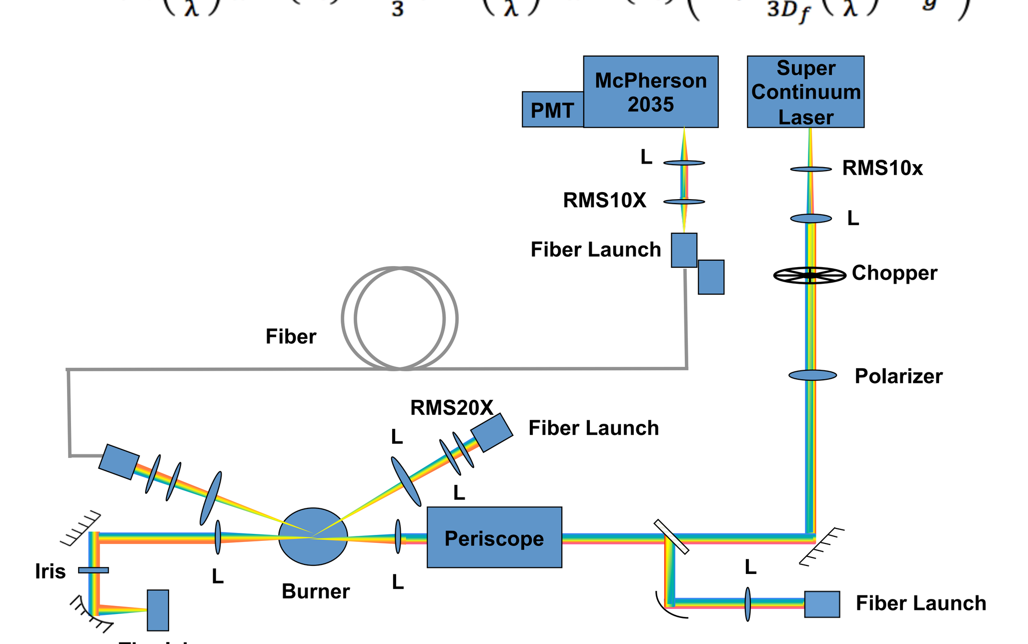


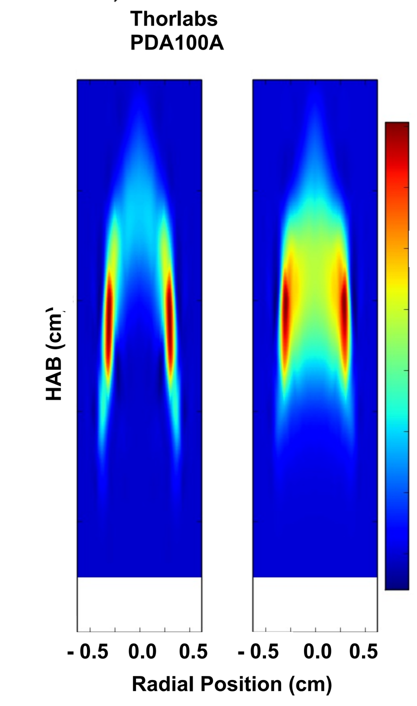
Journal of Aerosol Science 47 12-26 (2012).



Refractive Index	$m = n + ik$	Absorption	$\sigma_{abs}{}^{m} = -4\pi\left(\frac{2\pi}{\lambda}\right)a^3E(m)$
	$E(m) = Im\left[\frac{m^2-1}{m^2+1}\right]$		$\sigma_{abs}{}^{agg} = N\sigma_{abs}{}^{m}$
	$F(m) = \left\lvert\frac{m^2-1}{m^2+2}\right\rvert^2$	Total Scattering	$\sigma_{sca}{}^{m} = \frac{8}{3}\pi\left(\frac{2\pi}{\lambda}\right)^4 a^6F(m)$
Extinction	$-\ln\left(\frac{I}{I_0}\right) = \sigma_{ext}cl$		$\sigma_{sca}{}^{agg} = N^2\sigma_{sca}{}^{m}\,G(kR_g)$
	$\sigma_{ext}{}^{agg} = \sigma_{abs}{}^{agg} + \sigma_{sca}{}^{agg}$		$G(kR_g) = \left(1 + \frac{4}{3D_f}\left(\frac{2\pi}{\lambda}\right)^2 R_g{}^2\right)^{\frac{-D_f}{2}}$

$$\sigma_{ext}{}^{agg} = 4\pi N\left(\frac{2\pi}{\lambda}\right)a^3E(m) + \frac{8}{3}\pi N^2\left(\frac{2\pi}{\lambda}\right)^4 a^6F(m)\left(1 + \frac{4}{3D_f}\left(\frac{2\pi}{\lambda}\right)^2 R_g{}^2\right)^{\frac{-D_f}{2}}$$





- Normalized plots of scattering intensity at 30 degrees (left) and 160 degrees (right) in the 60% Ethylene-40%Nitrogen flame at 500nm.
- By expanding experiments to the full spectral range of 440nm to 600nm, Intensity versus wave vector plots will enable fractal parameters to be determined at each radial position.
- **Having both OBG and fractal parameter information as a function of flame position provides information about both the chemical and physical structure of soot particles throughout the flame.**