Experimental and computational determinations of optical band gaps for PAH and soot in N₂-diluted, ethylene/air non-premixed flames

Erin M. Adkins, Jennifer A. Herdman, and J. Houston Miller

Department of Chemistry, George Washington University

Simultaneous visible absorbance and scattering measurements are made at several heights above the fuel tube exit in a nitrogen-diluted, ethylene/air, non-premixed flame and this data was used to determine the optical band gap, as a function of radial position in the flame. This height was chosen as previous measurements in our laboratory have shown substantial Raman scattering from thermophoretically-sampled, carbonaceous material at this flame location. Further, this height is at the onset of large signal intensity in annular flame regions from laser-induced incandescence measurements. In our previous work, analysis of the Raman spectrum suggested the source of the scattering was PAH species with sp2 conjugation lengths of 1.0 – 1.2 nm, consistent with a molecular mass range of 500 -1000 Da. In a recent manuscript from our group, light from a light emitting diode, with center emission wavelength of 445 nm, was collimated, spatially filtered, and then focused into the flame. Transmitted light was recollimated and then directed into a spectrometer. After tomographic reconstruction of the radial extinction field, the optical band gap was derived from the near edge absorption spectrum using a Tauc analysis. The optical band gap, 2.38 ± 0.08 eV, was then compared with calculations of the electronic structure of a series of D₂h polynuclear aromatic hydrocarbon (PAH) using time-dependent density functional theory. HOMO-LUMO gaps for these PAH were correlated with the number of aromatic rings in the molecules. From this correlation, the measured band gap suggested that the source of the extinction could be a PAH with as few as 10 aromatic rings. In the current work, a super continuum light source is used to make simultaneous absorbance and scattering measurements. The super continuum light source is collimated and focused into a monochromator. The light is then split into light that is focused on the flame and light that bypasses the flame. The current system allows for adjustment of the scattering angle, wavelength, and polarization, while also allowing for the scattering to be accounted for in the Tauc analysis of the absorbance data. Initial results using the super continuum source are consistent with the results from the LED source, while offering better spectral resolution, more intensity, an extended spectral coverage, and additional information from scattering data.

1. Introduction
In the combustion of fossil or bio-derived fuels under rich conditions, some fraction of the fuel carbon is converted into fine particulate carbon. This carbonization process usually leads to “soot”, a form of amorphous carbon characterized by small primary particles aggregated into fractal structures. In a recent manuscript from our group, the predictions of “soot” concentrations from numerical simulations for nitrogen-diluted, ethylene-air flames were compared with laser-induced incandescence and Raman spectra observed from samples thermophoretically extracted using a rapid insertion technique (Herdman et al. 2011). In this
paper, our worked focused on an axisymmetric, non-premixed flame with a fuel of 60% ethylene in nitrogen. In some flame regions, the Raman spectra were obscured by intense radiation that appeared to peak in the near infrared spectral region. There was good agreement between spatial profiles of this *ex situ* laser-induced incandescence (ES-LII) and the "traditional" *in situ* laser-induced incandescence (IS-LII). Raman signatures were observed from low in the flame and extended into the upper flame regions. The spectra consisted of overlapping bands between 1000 and 2000 cm\(^{-1}\) dominated by the “G” band, near \(\approx 1580\) cm\(^{-1}\), and the “D” band in the upper 1300 cm\(^{-1}\) range. Because the Raman signals were observed at heights below those where *in situ*-LII was observed, we postulated that these signals were attributable to smaller particles. In our recent work, the \(I_D/I_G\) ratio varied only slightly when Raman was observed throughout the flame; from an approximate low of 0.9 to a high of 1.9, with the vast majority of the data observed between 1.0 and 1.4. Correlations of this quantity, for 785 nm excitation, with crystallite size suggest variations in the latter over a narrow range of \(\approx 1.0 - 1.2\) nm. As a hexagonal aromatic ring is \(\approx 0.25\) nm across, the lower end of this range would be equivalent to polynuclear aromatic hydrocarbon (PAH) that are 4 - 5 rings across. The data suggest that the Raman signal we observe is consistent with nascent particles that have a morphology dominated by modestly-sized PAH with masses in the 500-1000 Da range.

At the 34\(^{th}\) Symposium on Combustion held in 2102, we presented a study in which light from a light emitting diode, with center emission wavelength of 445 nm, was collimated, spatially filtered, and then focused into the flame. Transmitted light was recollimated and then directed into a spectrometer. After tomographic reconstruction of the radial extinction field, the optical band gap was derived from the near edge absorption spectrum using a Tauc analysis.

In the late 1960s, Tauc and coworkers demonstrated that the fall off in the absorbance at the near edge (i.e., long wavelength) of amorphous semiconductors provides a probe of localized states in the material (Wood and Tauc 1972). Specifically, the optical band gap, \(E_{\text{opt}}^g\), can be calculated from

(Eq. 1) \[ h\nu \cdot \alpha \approx (h\nu - E_{\text{opt}}^g)^r \]

where \(\alpha\) is the extinction coefficient, and \(r\) is often taken to be 2.

The optical band gap, \(\approx 2.4\) eV that we determined, was then compared with calculations of the electronic structure of a series of D\(_{2n}\) PAH using time-dependent density functional theory. HOMO-LUMO gaps for these PAH were correlated with the number of aromatic rings in the molecules. From this correlation, the measured band gap suggested that the source of the extinction could be a PAH with as few as 10 aromatic rings.

The 60\% C\(_2\)H\(_4\)/40\% N\(_2\) flame is one of a series of flames studied in the groups of Marshall Long and Mitchell Smooke at Yale (Smooke et al. 2004) and in our laboratory. As the nitrogen dilution is decreased from 68\% to 20\%, the amount of soot increases as predicted by both computations as well as experimental data quantifying the soot volume using two-dimensional laser-induced incandescence (LII) measurements (Mewes and Seitzman 1997, Quay et al. 1994, Vanderwal and Weiland 1994, Zhao and Ladommatos 1998) calibrated with an on-line extinction method (Axelsson, Collin and Bengtsson 2001).

In the current study, we wish to extend both our Raman and extinction measurements to the full set of flames described above. Particularly for the flames with larger soot content, it is important to distinguish the meaning of the terms "absorption" and "extinction". The measurement of light extinction (such as that provided in a simple UV/Vis absorption spectrophotometer) reports the sum of scattering and absorption, since both phenomenon attenuate the intensity of a light beam traveling across a medium (Bohren and Huffman 1983, Sorensen 1997, Kerker 1969). In performing the Tauc analysis described above, it is tempting to ascribe all of the extinction losses to absorption. However, Dobbins et al. noted that as much as 40\% of
extinction might be attributable to scattering losses in pure ethylene flames (with a peak volume fraction of ≈ 10 ppmv (Dobbins, Santoro and Semerjian 1991). We will show below how additional information from a scattering measurement is required to derive the contribution of absorption to total extinction and thus to perform the analysis of optical band gap.

1.2 Introduction to fractal agglomerate scattering and extinction


\[ N = k_o \cdot \left( \frac{R_g}{a} \right)^{D_f} \]  

(Eq. 2)

The latter quantities can be determined through measuring the dependence of scattering intensity on the wave vector, a function of both wavelength and observation angle (Souza and Miller 2012):

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

(Eq. 3)

For most of the last several decades, light scattering measurements have been performed with a single laser source (and usually one excitation wavelength) and either by collecting light at a single angle (Harding, Sattelle and Bloomfield 1992, Stover 1995, Yguerabide and Yguerabide 1998, Parkash et al. 1998, Trulson et al. 1998) or by making measurements at several angles (Koylu and Faeth 1994b, Koylu and Faeth 1994a, Bryant and Thomas 1995, Sorensen et al. 1992, Iyer et al. 2007). Both of these detection schemes have limitations. The first offers fast detection, but, generally, single angle detection cannot be used to differentiate between multiple particle sizes without being coupled to a particle separation technique, such as gel filtration or chromatography (Gabriel and McGuinness 1984, Korgel, Van Zanten and Monbouquette 1998, Machtle 1999, Qian, Mhatre and Krull 1997). The second scheme can provide good angle resolution and it can be used to differentiate between particles of various sizes without the need of a separation technique; however, this scheme is time consuming particularly if measurements are made at a great many angles (typically accomplished by placing a detector on a rotating stage).

For these measurements, we use a new wavelength-agile excitation source available in our laboratory. For decades, advances in photonic technologies have had an impact in sensing applications in fields ranging from biotechnology through industrial sensing. Among the more exciting recent developments has been the generation of “white light” in optical fibers. It has been observed for decades that “supercontinuum” generation will occur in a variety of materials when several nonlinear processes (including soliton fission, Raman and Brillouin scattering) result from excitation by an intense, narrow pump source (Hult 2007). These sources have found application in a range of fields including microscopy, telecommunication, and spectroscopy. Several commercial supercontinuum sources are on the market and typically use pulsed fiber lasers as the pump and photonic crystal fiber (PCF) as the “broadening” medium. By using excitation
wavelengths between 500 and 800 nm and monitoring at a fixed scattering angle of 90°, we can vary the wave vector between 0.01 and 0.02 nm\(^{-1}\), which falls between \(1/a\) and \(1/R_g\), the “Fractal” regime of scattering.

2. Methods
The experimental arrangement is shown in Figure 1. The light source used was a broadband super continuum laser (NKT Photonics SuperK Laser), which has wavelength dependent output over the range from 480 nm to 1750 nm. Emission from the laser was directed to a 600nm short pass filter (ThorLabs FES600) in order to direct light above 600nm out of the optical pathway and into a beam stop (ThorLabs LB1). The beam was then collimated and expanded, from 1.1mm to 11mm, using a lens system consisting of an Olympus microscope objective (Thorlabs RMS10x) and a 100 mm f.l. achromat mounted (ThorLabs AC254-100-A) in Thorlabs cage system. A flat mirror was used to direct the beam through a chopper (Stanford Research Systems SR540), an iris, and was then focused onto the monochromator using a 75mm f.l. achromat (ThorLabs AC254-75-A). The monochromator used was a McPherson Model 270 with a 1200 lines/mm grating blazed at 500nm. Using a 1000 \(\mu\)m slit width, the system provides approximately 2nm resolution over the experimental wavelength range. After passing through the monochromator, the beam passes through a 75mm f.l. acromat (ThorLabs AC254-100-A) and is focused onto a beam splitter (ThorLabs CM1-BS013). The beam splitter directs the light into a pathway that is directed through the flame and one that bypasses the flame, giving simultaneous measurement of the transmitted and incident light. The transmitted light branch is directed into the flame using flat mirrors and then focused into the center of the flame using 100mm f.l. lens.
The beam size at the focus was determined to be 0.33mm in the horizontal direction and 0.34mm in the vertically. Both the transmitted and incident light segments use a combination of a kinematically mounted flat mirror and a 100mm f.l. parabolic mirror (ThorLabs MPD254508-90-P01) to direct the beam onto a photodiode detector (transmitted light segment ThorLabs PDA100A, and incident light ThorLabs PDA10A) with a diffuser (ThorLabs DG10-600-MD) mounted on the front to focus light onto the detection surface. The incident light detector is connected to an analog lock-in amplifier (Princeton Applied Research 5209), where the transmitted light detector is connected to a digital lock-in amplifier (Stanford Research Systems SR850). The chopper, at 400 Hz, is used as the reference for both lock-in amplifiers and the output signal from the analog lock-in is digitized using a ADC on the digital lock-in amplifier. The data is then transmitted to a computer via the GPIB connection on the digital lock-in amplifier.

The flame studied was a nitrogen/diluter, ethylene/air, non-premixed flame supported on a burner designed and built at Yale University. Flames supported on this burner have been characterized by both our group and our collaborators at Yale using mass spectrometry, Raman, and laser-induced incandescence, as well as computationally using numerical simulations (Herdman et al. 2011) (Robertson 2001, Schnaiter et al. 2003, Bond and Bergstrom 2006). In these previous studies, a range of fuel mixture compositions have been studied, but here we only present data for a flame that was 80% ethylene/20% nitrogen by volume.

The burner consists of central fuel tube with an inner diameter of 0.4cm and a concentric air co-flow tube with an inner diameter of 5.1cm. The fuel velocity at the burner has a parabolic profile with an average velocity of 35cm/s with the air velocity profiles at the burner surface being plug flow of 35cm/s. This is maintained using a honeycomb cover over the region of the co-flowing air. The burner is placed on a stepper-motor controlled, translation stage (Velmax) that moves the burner horizontally and a manually-controlled translation stage for vertical movement.

3. Data Analysis

When line of sight extinction measurements are made through an axi-symmetric flame, the detected signal at any wavelength will have contributions from material at different temperature, concentrations, and densities through the region the radiation passes. The relationship between the signal contribution at a given wavelength and radial location, \( f(r, \lambda) \), and the intensity of a line of sight extinction signal, \( P(y, \lambda) \), collected across the axi-symmetric flame is expressed as:

\[
P(y, \lambda) = \ln\left(\frac{I_0}{I}\right)_{y,v} = 2 \int_0^y f(r, \lambda) dx
\]

To recover the radially-distributed data, a 3 point Abel inversion must be performed. In this work we adapt the approach reported by Dasch (Dasch 1992). Abel transformations have been used in past work by our group, for tunable diode laser absorption spectroscopy (Skaggs and Miller 1995) and on the Tauc extinction measurements using an LED (Miller et al. 2013). Here the deconvolved extinction signal, \( F(r_i, \lambda) \), is calculated from the line-of-sight data through

\[
F(r_i, \lambda) = \frac{1}{\Delta r} \sum_{j=0}^{\infty} D_{ij} P(y_j, \lambda)
\]

Where \( \Delta r \) is the spacing interval between each line-of-sight spectrum; the subscripts \( j \) and \( I \) are indices for the line-of-sight and radical coordinates, respectively; and \( D_{ij} \) is a matrix of linear operator coefficients determined by Dasch for a 3-point Abel inversion.

Because the Abel inversion procedure typically degrades the signal to noise ratio of the data, it is necessary to have centered, symmetric, and smooth profiles of projection data. In the past work, we have explored a
variety of data treatment techniques to prepare the raw experimental data for inversion including a variety of smoothing and fitting algorithms.

In this work, all data processing was done using the Enthought Python Distribution with an implementation of a Savitsky-Golay smoothing/filtering algorithm (Savitzky and Golay 1964) that builds on the SciPy open source framework (http://www.scipy.org/Cookbook/SavitzkyGolay).

4. Results, Discussion, and Future Plans
Figure 2 compares the tomographically reconstructed radial distribution of extinction with measurements of soot volume fraction by laser-induced incandescence. In general, the shape of the soot field is similar in both measurements with the first evidence of substantial particle concentrations at approximately 10 mm above the burner’s surface. However, these annular regions do not appear to be as spatially narrow in the extinction measurements, which might be partially attributable to the reconstruction algorithm as well as the inherently lower spatial resolution in the extinction measurements. (The beam waist at the focus above the burner was 0.33 mm and the lateral spacing between projection data points was 0.5 mm).

Figure 2. Contours of soot volume fraction as measured by laser-induced incandescence and radial extinction coefficients collected with 530 nm radiation from the supercontinuum source.
In the coming months, we will be adding the scattering channel’s data at several excitation wavelengths. Building on the detailed analysis laid out in Iyer et al. (Iyer et al. 2007), we will be able to extract from the combined measurements of extinction and scattering intensity as a function of wave vector determinations of primary particle size, number of primary particles per aggregate, and volume fraction. More importantly, we will determine the fraction of extinction attributable to absorption which will enable the determination of optical band gap as a function of height in eth flame and in the full range of nitrogen-diluted, ethylene flames.

Acknowledgements

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

References
