Constancy of soot refractive index absorption function: Implications for optical measurements of nanoparticles

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1. Introduction

The emission of carbonaceous particles (soot) in the atmosphere constitutes a serious concern for both human health and environment. Therefore recent research and development in the area of combustion have been motivated by the need to understand the mechanism of soot formation in practical combustion devices and to quantify soot emission. Conventional methods for soot emission estimation, such as gravimetric sampling and measurement of smoke number, have deficiencies in sensitivity and temporal resolution. Meanwhile, different optical diagnostic techniques have been developed and proved to be particularly suitable for the combustion environment. These methods can offer remote, non intrusive, *in situ*, spatially and temporally precise measurements of important parameters including soot concentration and morphology. In particular, the two-color method has been widely used in diesel engines in order to measure flame temperature and KL factor, which is proportional to the soot concentration. The light extinction technique has also been a popular and accurate way to measure soot concentration, and combined with light scattering can be used to measure soot particle size. The Laser-Induced Incandescence (LII) technique has emerged as an attractive method for real-time soot concentration monitoring in practical devices [1]. This technique has been extensively used to measure soot particulate emissions from diesel and gasoline engines and from gas turbines, soot concentrations in laboratory flames, and black carbon in the ambient environment.

The interpretation of soot optical diagnostics requires the knowledge of the optical properties of soot. These properties, in particular the propensity of soot to absorb and scatter light, are exploited by most of the commercially available instruments developed to evaluate the aerosol light absorbing emission. These instruments implement filter-based (absorption or reflectance), photoacoustic, refractive-index-based, extinction-scattering, or LII techniques [2], and therefore the measured particulate concentrations are affected by the soot optical properties used for the evaluation.

Many studies of soot optical properties are presented in the literature, but they show large uncertainties and discrepancies. In many cases the optical properties of mature, post-flame soot are used to evaluate soot optical measurements in any kind of combustion environment. Nevertheless different types of carbonaceous particles are produce during combustion processes and they might have different optical properties which vary with aging, which refers to the maturity of the soot from its first inception in the flame, through solidification, surface growth, aggregation, oxidation, cooling,emission from the combustion process, and subsequent atmospheric processing [3].

In the present work, spectrally resolved line-of-sight attenuation (Spec-LOSA) measurements have been performed to evaluate the spectral variation of the refractive index absorption function in an ethylene/air premixed flame. The flame, a McKenna burner, is considered one-dimensional, essentially uniform in the radial direction, with soot age varying with height. This flame is highly relevant to practical combustion devices since it produces particulate matter of similar size and composition, as recently reported by D'Anna [4]. We show that the measured refractive index dependent absorption function, $E(m)_\lambda$, which potentially includes effects of non-soot light absorbing constituents, has a very strong spectral dependence which varies with height above the burner.

2. Theory

In line-of-sight-attenuation (LOSA) measurements, according to the Beer-Bouger-Lambert law, the optical transmissivity of an aerosol is measured along a linear path through the medium and is functionally related to a line integral of the local extinction coefficients, $K_\lambda^{(e)}$, along the path via:

$$\tau_\lambda = \frac{I_\lambda}{I_{\lambda,0}} = \exp\left(\int_{-\infty}^{\infty} K_\lambda^{(e)} ds\right) \tag{1}$$

where τ_λ is the transmittivity of the medium, $I_{\lambda,0}$ is the incident light intensity, I_λ is the transmitted one and s is the spatial location along the path. If the medium is uniform along the line-of-sight, Eq. 1 simplifies to:

$$-\ln\tau_\lambda(y) = K_\lambda^{(e)}L \tag{2}$$

where L is the length of the chord through the medium. For a horizontal chord through the centreline of a McKenna burner this simplification is approximately true.

According to RDG-FA (Rayleigh-Debye-Gans– Fractal Aggregate) theory for fractal aggregates made up of primary particles that fall in the Rayleigh range (i.e. $\pi d_p/\lambda < 0.3$, where d_p is the diameter of a primary particle), soot concentration, f_v, is related to the extinction, absorption and scattering coefficients as:

$$f_v = \frac{K_\lambda^{(a)}\lambda}{6\pi E(m)_\lambda} = \frac{K_\lambda^{(e)}\lambda}{6\pi(1+\rho_{sa,\lambda})E(m)_\lambda} \tag{3}$$

where $\rho_{sa,\lambda}$ is the ratio of the total scatter coefficient (over 4*π steradian), $K_\lambda^{(s)}$, to the absorption coefficient, $K_\lambda^{(a)}$. The scatter coefficient can be estimated via RDG-FA theory if soot morphology is known (e.g. the primary particle diameter and number of particles per aggregate). In circumstances where light scatter is negligible (i.e. for very small soot aggregates) or for soot of known morphology, Spec-LOSA provides a valuable tool to investigate the relative variation of $E(m)$ with λ:

$$E(m)_\lambda = \frac{K_\lambda^{(a)}\lambda}{6\pi f_v} \propto K_\lambda^{(a)}\lambda \sim K_\lambda^{(e)}\lambda \tag{4}$$

since f_v is constant in a given measurement. Absolute measurement of $E(m)_\lambda$ is possible if f_v can be unequivocally measured by another method, such as gravimetric sampling. Note that in the above analysis, it is implicitly assumed that soot is the only constituent in the optical path that is absorbing light.

3. Apparatus

The experimental apparatus is shown schematically in Figure 1. An intense diffuse light produced by an Hg arc lamp was focused on to the flame and the transmitted intensity was collected on the vertical entrance slit of a spectrometer. In order to provide a reference measurement of the lamp intensity before transmission through the flame, the light beam was split into two paths by means of an optical wedge: the primary optical path passing through the center axis of the flame, while the secondary optical path bypasses the flame. The location on the entrance slit was shifted vertically for one beam such that two signals, the lamp (our light source) and the transmission (both the lamp and the flame) were collected simultaneously. In this way any variation in lamp output intensity during the acquisition period was captured. The spectrometer was configured to measure over the wavelength range of 450 to 800 nm. This range was selected to optimize the combination of the output intensity of the lamp and the sensitivity of the detector, while avoiding second order effects in the spectrometer. The CCD attached to the output plane of the spectrometer records the two signals on one axis and wavelength on the orthogonal axis.
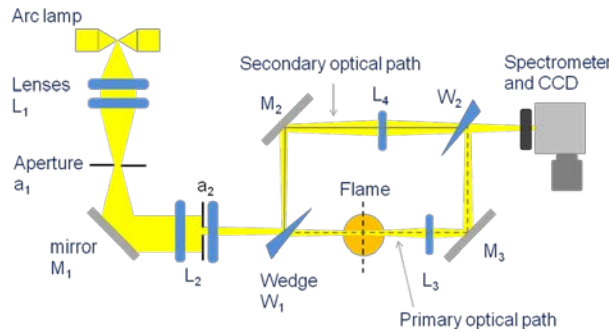

Figure 1: Schematic of Spec-LOSA diagnostic

A transmissivity measurement is typically achieved from a sequence of four measurements. These are the detected intensity of the lamp without the attenuation medium present (*lamp*), the intensity measured in the absence of lamp and attenuating medium (*dark*), the intensity with both the lamp and attenuating medium (*transmission*), and the intensity measured from the attenuating medium in the absence of the lamp (*emission*). The transmissivity is then

calculated as $\tau_\lambda = (transmission - emission)/(lamp\text{-}dark)$. At each measurement height, image sets consisted of 20 shot acquisitions for each measurement (*i.e.*, *lamp*, *dark*, *transmission* and *emission*) averaged to reduce shot noise.

An ethylene/air premixed flame was used in these experiments. The flame was produced on a bronze porous plug McKenna burner (inner-plug diameter 60 mm) at atmospheric pressure. The total fuel/air flow rate was 10 l/min and the equivalence ratio was 2.1. To shield the flame from the surrounding air, an external shroud of nitrogen, flowing at 15 l/min, was used. Moreover, for flame stabilization, a stainless steel plate of 60 mm diameter was placed at 21 mm above the burner. Spec-LOSA measurements were performed at a range of heights above the burner (HAB) surface, from 6 to 16 mm, in order to follow the soot inception, growth, and other in-flame aging processes.

A typical set of averaged images is shown in Figure 2, along with the transmissivity calculated from these images.
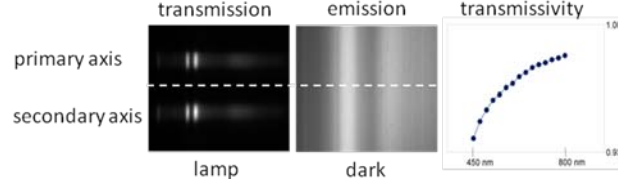

Figure 2: Spec-LOSA measurements in ethylene/air premixed flame, 20 shot averages, HAB = 12 mm

The horizontal axis of each image is the spectral axis. The upper spectrum in each image represents the intensity from the primary optical path (i.e. the light passing through the flame) and the lower spectrum is the secondary optical path.

4. Results

The spectral variation of the transmissivity at different heights above the burner is illustrated in Figure 3(a), showing the spectral variation of the measurements and the strong increasing light attenuation with increasing height in the flame. The greatest attenuation occurs at the shortest wavelengths.
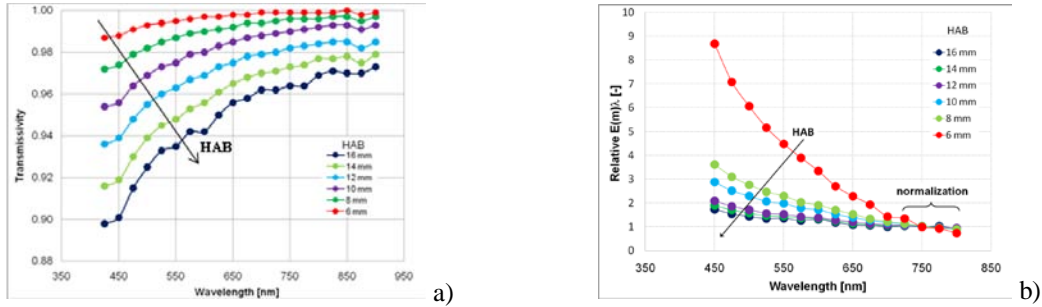

Figure 3: Transmissivity (a) and relative $E(m)_\lambda$ (b) at different heights above the burner

Since the McKenna burner is quasi one-dimensional only a single line-of-sight measurement through the burner centreline was made at each height and a line integrated extinction coefficient was evaluated via Eq.(2). When multiplied by the measurement wavelength, this quantity is proportional to the soot refractive index absorption function, $E(m)_\lambda$, if light scattering by the aggregates is small relative to light absorption. To gain information on soot morphology, thermophoretic sampling and transmission electron microscopy (TEM) analysis were performed. Soot morphology parameters were measured and the correction for scattering has been evaluated as negligible [5].

Figure 3(b) shows the relative $E(m)_\lambda$ behaviour as a function of HAB, where the data at each height is normalized to average $E(m)$ at the upper wavelengths (725-800 nm). The relative $E(m)_\lambda$ is highly variant with wavelength at all the heights above the burner. The slope of the curves is greater lower down in the flame, reaching an eight-fold variation at HAB = 6 mm over the range 450 nm to 800 nm. However, even at the height of 16 mm, the variation is still 45%. Nevertheless the results at all heights level to an almost constant value at the upper visible region of the spectrum. Thus, the common assumption that attenuation or emission measurements in the upper visible or near infrared regions of the spectrum will avoid interferences from PAH or non-soot nanoparticles, or other possible uncertainties in soot optical properties is confirmed under these flame conditions.

The source of the variation of relative $E(m)_\lambda$ with height above burner is uncertain. Attenuation may come from large PAH molecules, semi-transparent soot precursor nanoparticles, brown carbon, or black carbon. Each would have different spectral absorption tendencies and the overall relative $E(m)_\lambda$ variation could simply track the dominance of each class of absorber in the overall mixture as a function of height. Equally, particles in each class of absorbing species could be evolving such that their spectral characteristics change with height.

Whether the detected attenuation comes from soot or non-soot species, this observation has significant implications for all soot optical diagnostics. For soot spectral emission measurements, the influence is quite dramatic. Assuming a constant $E(m)_\lambda$ can lead one to over-predict the soot temperature by 200-300 K and to significantly under-predict the soot volume fraction (as much as 70%). The implication of a varying relative $E(m)_\lambda$ for other optical techniques, such as LII, is less clear. While large PAHs and nanoparticles could contribute to attenuation and possibly to emission signals, it is less likely that they could be laser-heated to the same peak temperatures as soot without evaporating or sublimating and therefore would likely make a small contribution to the total LII emission signal. Conversely, if the particles are comprised of brown carbon (i.e. immature or high hydrogen content soot), attribution of an appropriate $E(m)_\lambda$ to the soot during LII signal analysis would be difficult and errors would propagate in a similar fashion to two-colour flame emission measurements.

5. Summary

It is evident from the current measurements that there is a great deal of uncertainty surrounding the correct soot refractive index absorption function to use when interpreting light absorption and emission measurements from soot and other absorbing/emitting species in a McKenna burner. This behaviour is critical to the correct interpretation of soot spectral emission measurements and makes measurements essentially impossible without *a priori* knowledge of the relative $E(m)_\lambda$ function at the measurement location. Nevertheless, it should be noted that while this is true for the flame conditions investigated, it is difficult to predict how that can be extended to other flame conditions, and other sources of soot, including post-flame soot.

The results do indicate that as soot ages in the flame, the optical properties change. Care should be taken when calculations depend upon soot optical properties, as literature data for these properties may have been acquired under significantly different conditions than the intended application, and are likely to lead to significant errors. For instruments dependent upon aspects of optical measurements, researchers should be aware that the calibration of the instrument may vary as the soot being measured varies in properties.

Future research will include LII measurements collected in the same flame with the objective of clarifying the contribution of non-soot species to the absorption and to LII measurements, and to correct LII measurement interpretation.

6. References

[1]   H. Zhao, Ladommatos N., Prog. Energy Combust. Sci. 24 (1998) 221-255.
[2]   H. Moosmüller, R.K. Chakrabarty, W.P. Arnott, J. Quant. Spectrosc. Radiant. Transfer 110 (2009) 844-878.
[3]   T.C. Bond, R.W. Bergstrom, Aerosol Sci. Technol. 40 (2006) 27-67.
[4]   A. D'Anna, Proc. Combust. Inst. 32 (2009) 593-613.
[5]   F. Migliorini, K.A. Thomson, G.J. Smallwood, Proceedings of Combustion Institute Canadian Section Spring Technical Meeting, Ottawa, ON, May 9-12, 2010.

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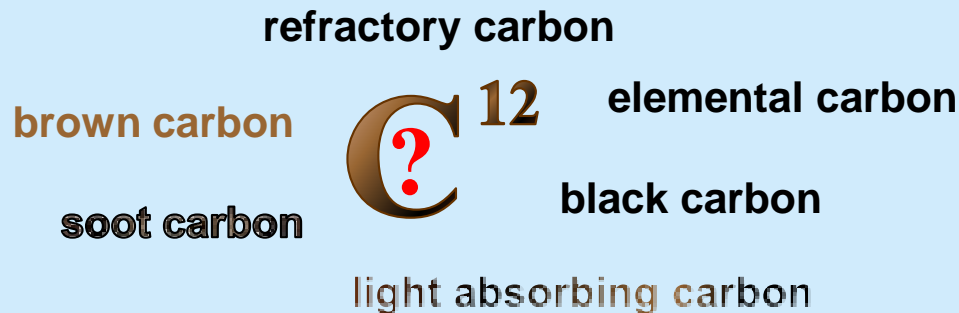
Rationale

- The quantification of <u>soot</u> emission is a concern for

Health

Environment

refractory carbon

brown carbon

C^{12}

?

elemental carbon

soot carbon

black carbon

light absorbing carbon

- Effect on the performance of the combustion processes
- Need diagnostic for in-situ and ambient monitoring
- Optical diagnostics are attractive, non-intrusive method to measure, understand and hopefully control soot formation
  - validation for combustion and soot formation modeling
  - real-time feedback for combustor optimization

Soot diagnostics in diesel engines

<u>Optical techniques</u>

Technique	Principals	Information
Two-color pyrometry	thermal radiation from soot particles	Soot temperature and soot concentration
Light extinction	attenuation of light by scattering and absorption by the particles	Soot concentration
Light scattering	measure the amount of light scattered by the particles	Soot particle size
Laser-Induced Incandescence (LII)	energy absorption and heat loss from the particle	Soot volume fraction and soot particle size

Zhao H., Ladommatos N., Prog. Energy Combust. Sci. 24, 1998

⇨ All based on the absorption properties of soot particles

Measurements of aerosol light absorption

Filter-based techniques

measure the optical attenuation through a filter on which aerosol particles have been accumulated

⇨

- Filter transmittance method
- Filter reflectance method
- Multi-Angle Absorption Photometry

Instrument name	Company	Principle
Aethalometer	Magee Scientific Company	Black Carbon density from real time filter transmission
Particle Soot Absorption Photometer	Radiance Research Inc.	Aerosol absorption coefficient from real time filter transmission
Multi-Angle Absorption Photometer (MAAP)	Thermo Fisher Scientific	Aerosol absorption coefficient, Black Carbon mass density from real time filter transmission with scattering correction

Moosmüller H., Chakrabarty R.K., Arnott W.P., J. Quant. Spectrosc. Radiat. Transfer 110 (2009) 844-878

14th ETH Conference on Combustion Generated Nanoparticles, Zurich, August 1-4, 2010

Measurements of aerosol light absorption

In situ measurements

- Photoacoustic technique
- Refractive index-based technique
- Scattering-extinction
- LII

acoustic measurement of the heat generated from aerosol light absorption, and its transfer to the surrounding air.

modulation of the refractive index of the air surrounding the heated particle

Instrument name	Company	Principle
Micro Soot Sensor	AVL LIST GMBH	Black Carbon density from real time, in-situ photoacoustic signal
Photo-Acoustic Soot Spectrometer	Droplet Measurements Technologies	Aerosol absorption coefficient from real time,in-situ photoacoustic signal
Single Particle Soot Photometer	Droplet Measurements Technologies	Black Carbon mass of individual particles from LII
LII 300	Artium Technologies	Soot concentration, specific surface area and primary particle diameter in real-time

Moosmüller H., Chakrabarty R.K., Arnott W.P., J. Quant. Spectrosc. Radiat. Transfer 110 (2009) 844-878

Optical Properties in Soot Diagnostics

The interpretation of most of these diagnostics, and in particular all the optical ones requires knowledge of the <u>optical properties of soot</u>.

The key parameters are:

- ✓ **E(m)**: soot refractive index absorption function
- ✓ **F(m)**: soot refractive index scattering function

Lots of studies on soot optical properties in the literature

Quite significant spread in $E(m)_\lambda$

<u>Post flame soot</u>: quite consistent optical properties

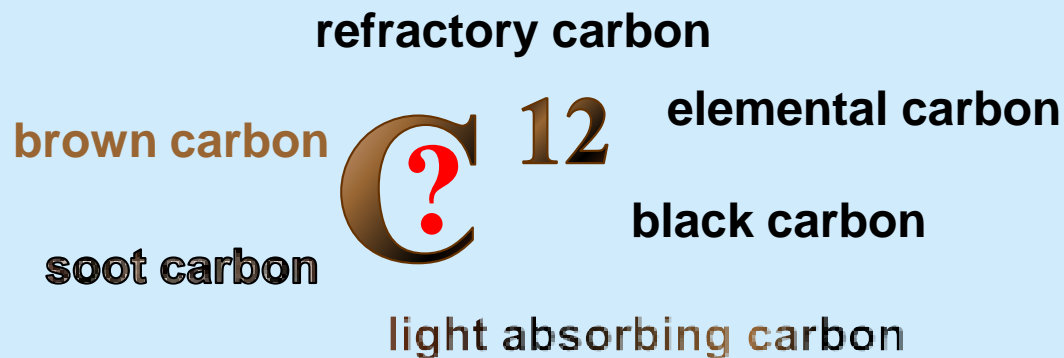↳ $E(m)_\lambda$ **invariant with wavelength**

<u>In-flame soot</u>: confusing and sometimes contradictory observations

Soot optical properties in the literature

Key observation:

various definitions exist for carbon particles produced during combustion processes

refractory carbon

brown carbon

C?**12** elemental carbon

black carbon

soot carbon

light absorbing carbon

⇨ Different spectral dependence of light absorption
{
Residence time
H/C ratio
Burner type
Fuel nature
Soot age
}

Soot optical properties in the literature

90's: Existence of 2-4 nm non-soot nanoparticles in flames

	D'Alessio et al.[1]	Dobbins et al.[2]
Structure	polymer-like structures , 2-3 aromatic rings	layers of fully condensed large PAHs
Absorption properties	strong absorbers in the UV transparent in the visible	visible absorbers

[1] A. D'Alessio, A. D'Anna, A. D'Orsi, P. Minutolo, R. Barbella, A. Ciajolo, Proc. Combust. Inst. 24 (1992) 973-980.
[2] R.A. Dobbins, R.A. Fletcher, W. Lu, Combust. Flame 100 (1995) 301-309.

Objective

- Investigation of soot optical properties of <u>in-flame</u> soot

- Measure the 'relative' variation of $E(m)_\lambda$ with wavelength for soot of differing 'ages' in a laminar premixed flame

⇩

Multi-wavelength line-of-sight attenuation (SpecLOSA) measurements

SpecLOSA
Governing equations

- transmissivity of a medium (τ_λ) can be related to the extinction coefficient of the material in the medium ($K^{(e)}_\lambda$) as:

$$\tau_\lambda = \frac{I_\lambda}{I_{\lambda,0}} = \exp\left(-\int_{-\infty}^{\infty} K^{(e)}_\lambda ds\right)$$

(Lambert-Beer law)

- if the medium is uniform along the line-of-sight:

$$-\ln \tau_\lambda = K^{(e)}_\lambda L$$

L: length of the chord through the medium

- if measurements performed at many wavelengths, can determine $K^{(e)}_\lambda$ as a function of wavelength

- E(m)$_\lambda$ is related to $K^{(e)}{}_\lambda$ via the soot volume fraction f_v as:

$$f_v = \frac{K_\lambda^{(a)}}{6\pi E(m)_\lambda} = \frac{K_\lambda^{(e)}\lambda}{6\pi(1+\rho_{sa,\lambda})E(m)_\lambda}$$

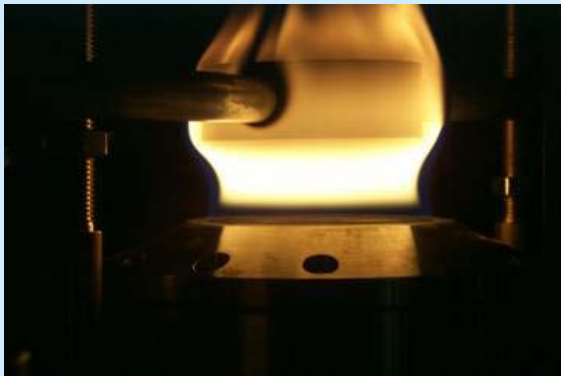$\rho_{sa,\lambda}$ is the ratio of scatter coefficient to absorption coefficient

- If light scatter is negligible or for soot of known morphology, rearranging:

$$E(m)_\lambda = \frac{K_\lambda^{(a)}\lambda}{6\pi f_v} \propto K_\lambda^{(a)}\lambda \approx \frac{K_\lambda^{(e)}\lambda}{(1+\rho_{sa})} \propto -\ln(\tau)\lambda$$

! we implicitly assumed that soot is the only constituent in the optical path absorbing light

Bronze Mckenna burner

- Widely used in the literature
- The flame is considered as a standard in the lean and close-to-stoichiometric conditions
- The flame is designed and assumed to be one-dimensional, which allows simplified combustion modeling
- Soot ages with the height in the flame
- Used as a standard for the development of the laser-induced incandescence (LII) technique

Ethylene/air mixture:
$\Phi = 2.1$, total fuel/air flow rate = 10 l/min,
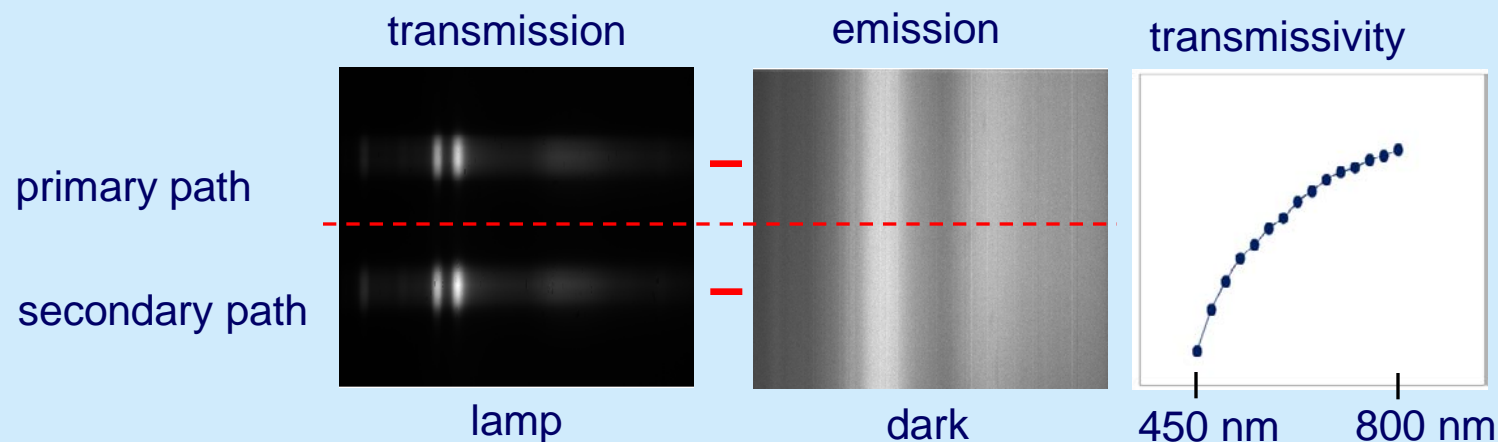N_2 shroud = 15 l/min, stabilization plate @ 21 mm
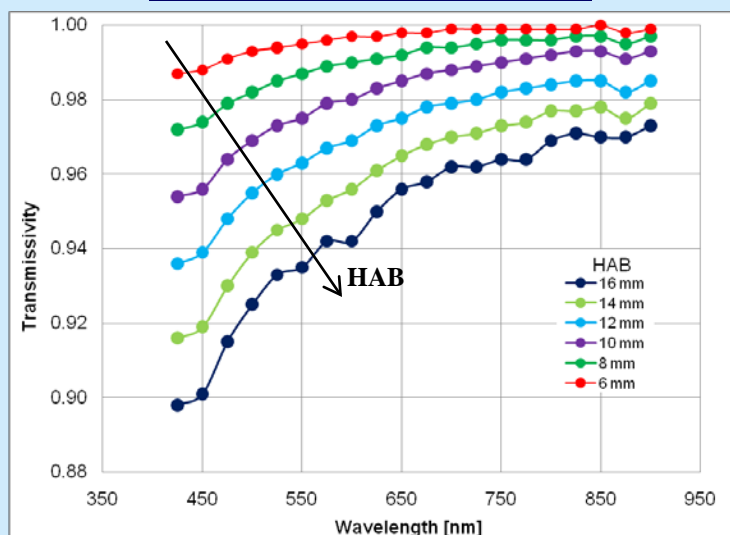
Zero-dimensional Spec-LOSA
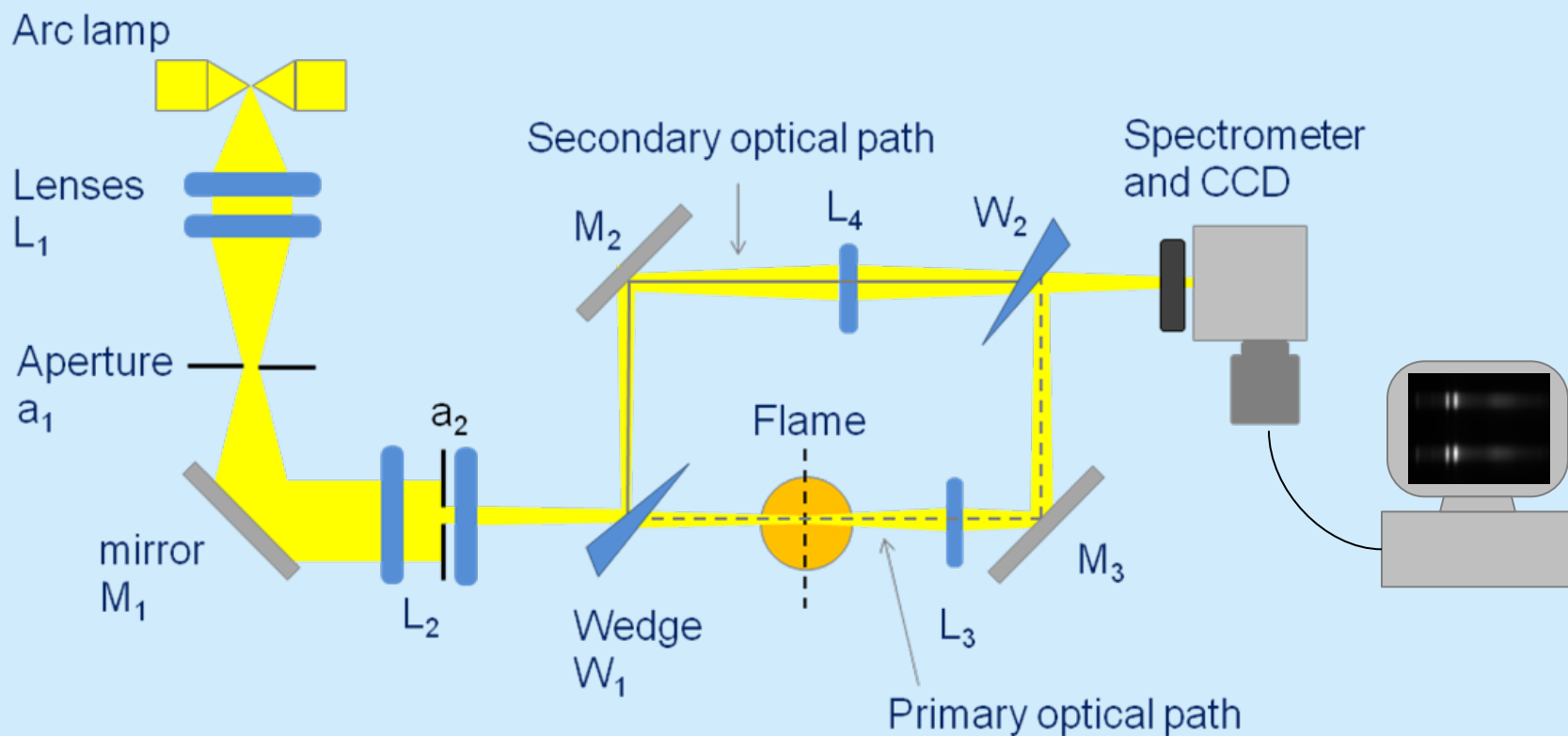
Transmissivity

$$transmissivity = \frac{transmission - emission}{lamp - dark}$$

transmission

emission

transmissivity

primary path

secondary path

lamp

dark

450 nm   800 nm

Transmissivity

- strong increasing of light attenuation with increasing height above the burner
- the greatest attenuation occurs at the shortest wavelengths
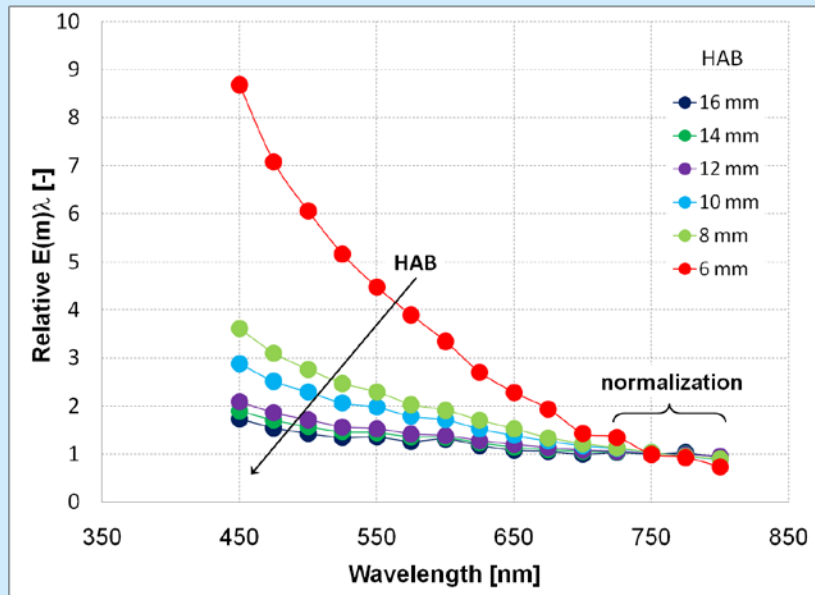- this variation suggest a change in the structure or composition of the absorbers

If light scattering by the aggregates is small relative to light absorption:

$$E(m)_\lambda \propto -\ln(\tau)\lambda$$

⇨ Scattering contribution from thermophoretic sampling and TEM analysis:

Negligible scattering

Relative E(m)$_\lambda$ variation in a Premixed flame

The relative *E(m)$_\lambda$* is NOT flat

- The slope is greater low down in the flame
- The curves level to an almost constant value at 750

⇨ PAHs/non-soot species are more likely to absorb at lower visible wavelengths

- **Strong variation** of $E(m)_\lambda$ with $\boldsymbol{\lambda}$ and with **height above burner**

- Similar behavior has been observed in a preliminary work on an ethylene diffusion flame (65 mm visible height):

  @ 42 mm: up to 15% variation in the low visible,

  almost constant above 650 nm

- Could indicate strong variation of soot optical properties with **soot age**

- Could also be absorption form **large PAHs, semi-transparent soot precursor nanoparticles, brown carbon, black carbon**…

- Significant implications for two-color pyrometry:

  - **constant E(m)$_\lambda$**
  - T_0 = 1800 K
  - λ_{det}: 450 and 800 nm

HAB [mm]	T_{soot}	f_v
6	⬆ 450 K	⬇ 88 %
12	⬆ 200 K	⬇ 63 %

- The implication for other optical absorbing techniques are not easy to predict:

  - do PAHs and nanoparticles participate?

  - influence of brown carbon or soot in different aging status?

- Big uncertainties exist for the soot refractive index absorption function to use when interpreting optical measurement in a premixed flame

  - do similar uncertainties exist for post-flame soot?

Future Work

- Multi-wavelength emission measurements to determine if multi-wavelength pyrometry agrees with multi-wavelength attenuation

- LII to determine sensitivity of LII to aging soot and non-soot mix

Acknowledgements

- NRC/Helmholtz collaboration

Thank you for your attention!

Artium Technologies Instruments

Artium Technologies takes an active role, with NRC's support, in working with customers who have purchased the LII 300 (top) or LII 200 (bottom) instruments

- Easy to use
- Low maintenance system
- Low operating costs
- **Very high sensitivity**
- **Compact rugged and portable instrument**
- Built-in computer and display, touchscreen control
- **Completely enclosed laser, optics, and sampling cell**
- Built-in pneumatics controller and sampling system
- Includes real-time pressure and temperature measurements to reduce data to STP
- Fail safe valve prevents sample from entering cell if purge air or power are off
- **Technologies protected by US Patents 6,154,277 and 6,181,419 under license from National Research Council (NRC) Canada**