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Optical Properties of Laser Heated Soot Aggregates

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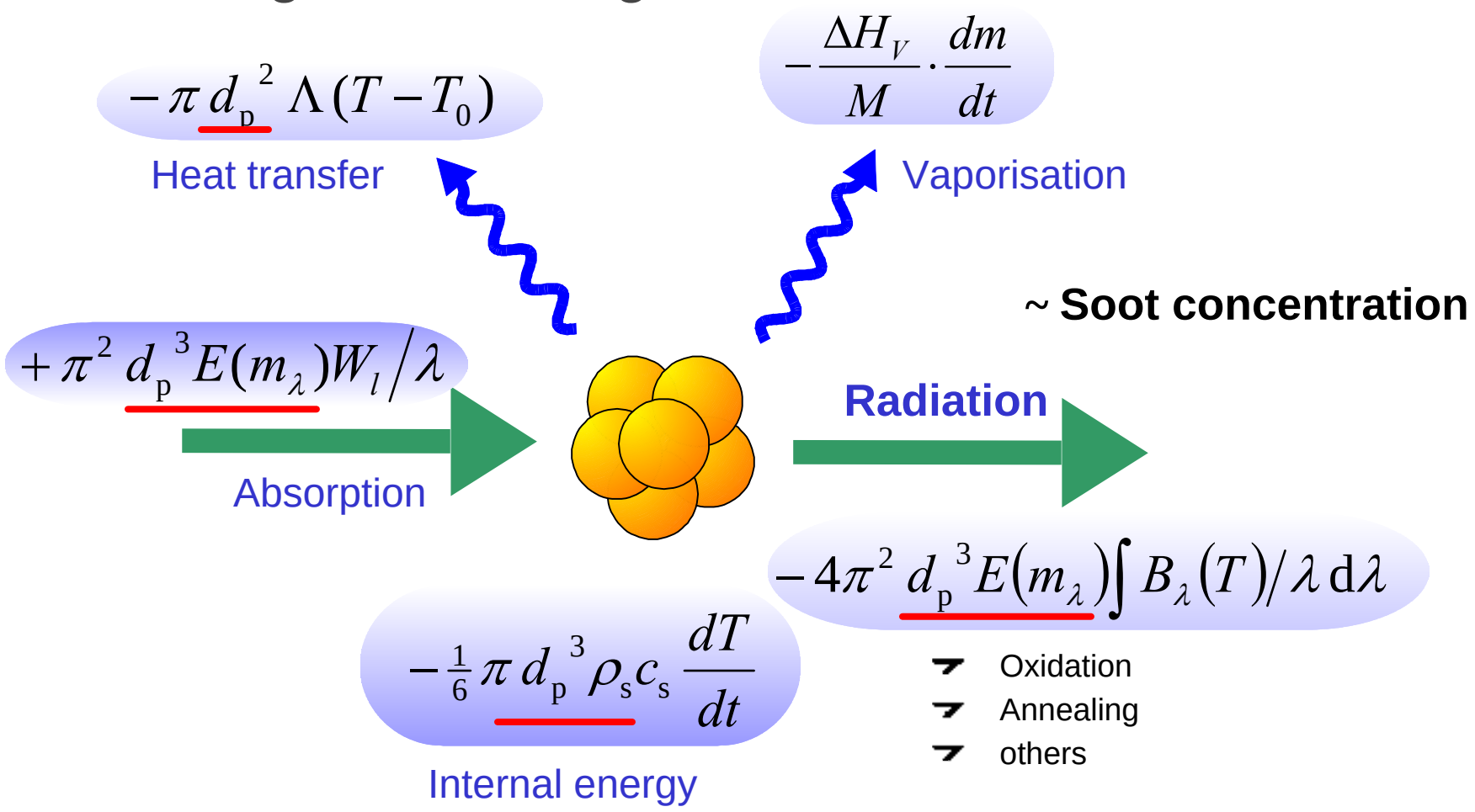
Introduction

- Key premises of Laser Induced Incandescence (LII) is that light emission properties of soot are:
  a) Predictable
  b) Not influenced by rapid laser heating of soot
     - From ambient to ~4000 K in less than 10 nanoseconds!
- Why do we care?
  – If emission not predictable, then we can't make sense of LII emission measurements
- This study aims to answer questions about how rapid heating influences the optical/light emitting properties of soot

Model of heat transfer to and from soot aggregates during laser heating



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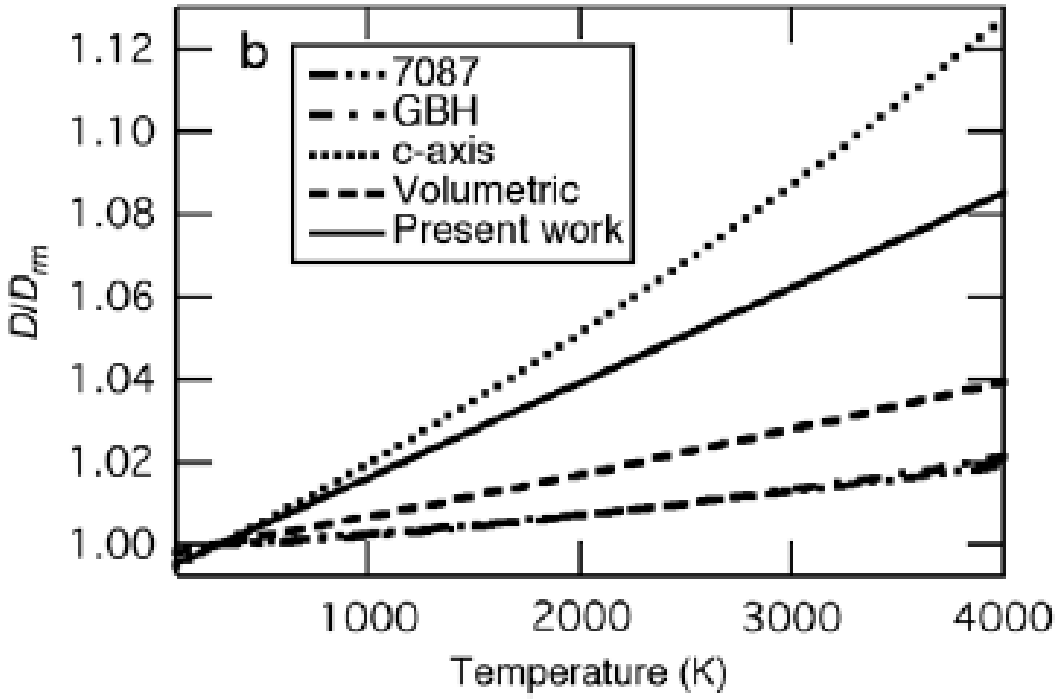
Soot expansion with temperature

Michelsen et al., *Carbon* **48**, 2175-2191 (2010)



- Complex internal structure of soot makes density modeling difficult
- Diameter change from 2 to 12% expected when heated to 4000K
- Volume change of 6 to 40%!

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Strategy

- Line-of-sight attenuation (LOSA) to monitor variation in the extinction coefficient of soot during laser heating
  - Extinction good surrogate for absorption coefficient
  - Measure at 405 and 830 nm
    - Close to wavelengths used in LII emission detection
  - Measure for a range of laser fluences
    - 0.28 to 4.0 mJ/mm^2
- Measure elastic light scattering from soot during laser heating
  - Measure scattering of 1064 nm (laser used to heat soot)

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Theory – emission and absorption

- Light emission and absorption propensity of soot

$$K_{\mathrm{abs},\lambda} = N_{\mathrm{p}} \frac{\pi^2 {d_{\mathrm{p}}}^3 E(m_\lambda)}{\lambda}$$

- Line-of-sight attenuation (transmissivity)

$$\tau(t) = I_\lambda(t) / I_{\lambda,0} = \exp\left(-K_{\mathrm{ext},\lambda}(t) L\right)$$

$$K_{\mathrm{ext},\lambda}(t) = -\ln\left(I_\lambda(t) / I_{\lambda,0}\right) / L$$

$$K_{\mathrm{ext},\lambda} = K_{\mathrm{abs},\lambda} + K_{\mathrm{sca},\lambda} \approx K_{\mathrm{abs},\lambda}$$

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Theory – scattering

- Light scattering propensity of soot aggregates

$$K_{\mathrm{sca},\lambda}^{\mathrm{agg}}(\theta) = N_{\mathrm{agg}} C_{\mathrm{sca},\lambda}^{\mathrm{p}} \int N^2 P(N) S\left(4\pi \sin(\theta/2)/\lambda\right) \mathrm{d}N$$

$$C_{\mathrm{sca},\lambda}^{\mathrm{p}} = k^4 \left(\mathrm{d_p}/2\right)^6 F(m_\lambda)$$

- Scattering intensity measurements

$$I_{\mathrm{sca},\lambda}(\theta) = I_{laser} K_{\mathrm{sca},\lambda}^{\mathrm{agg}}(\theta)$$

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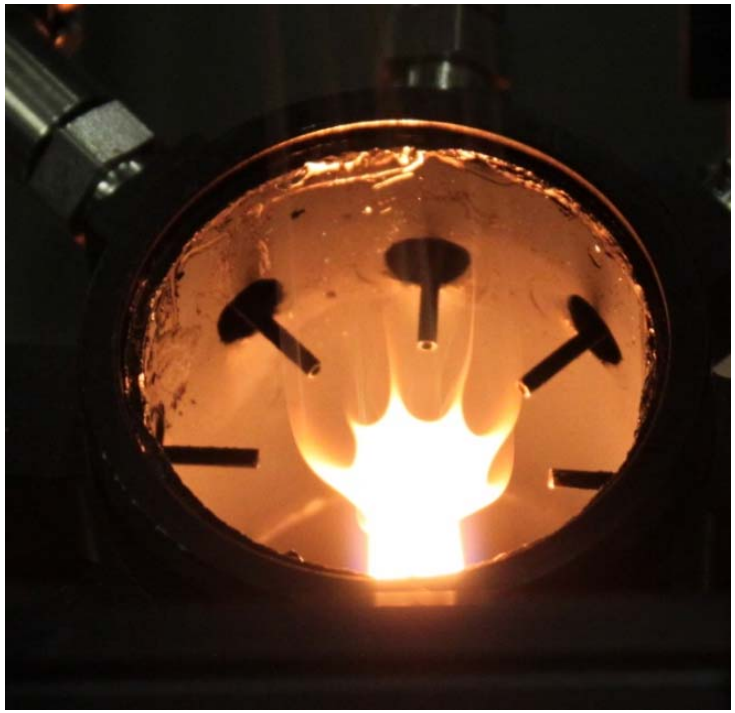
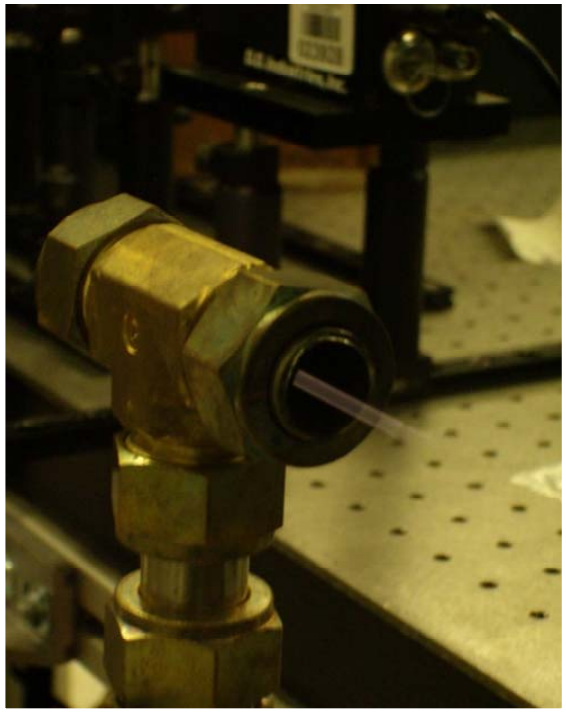
Apparatus – Soot Source





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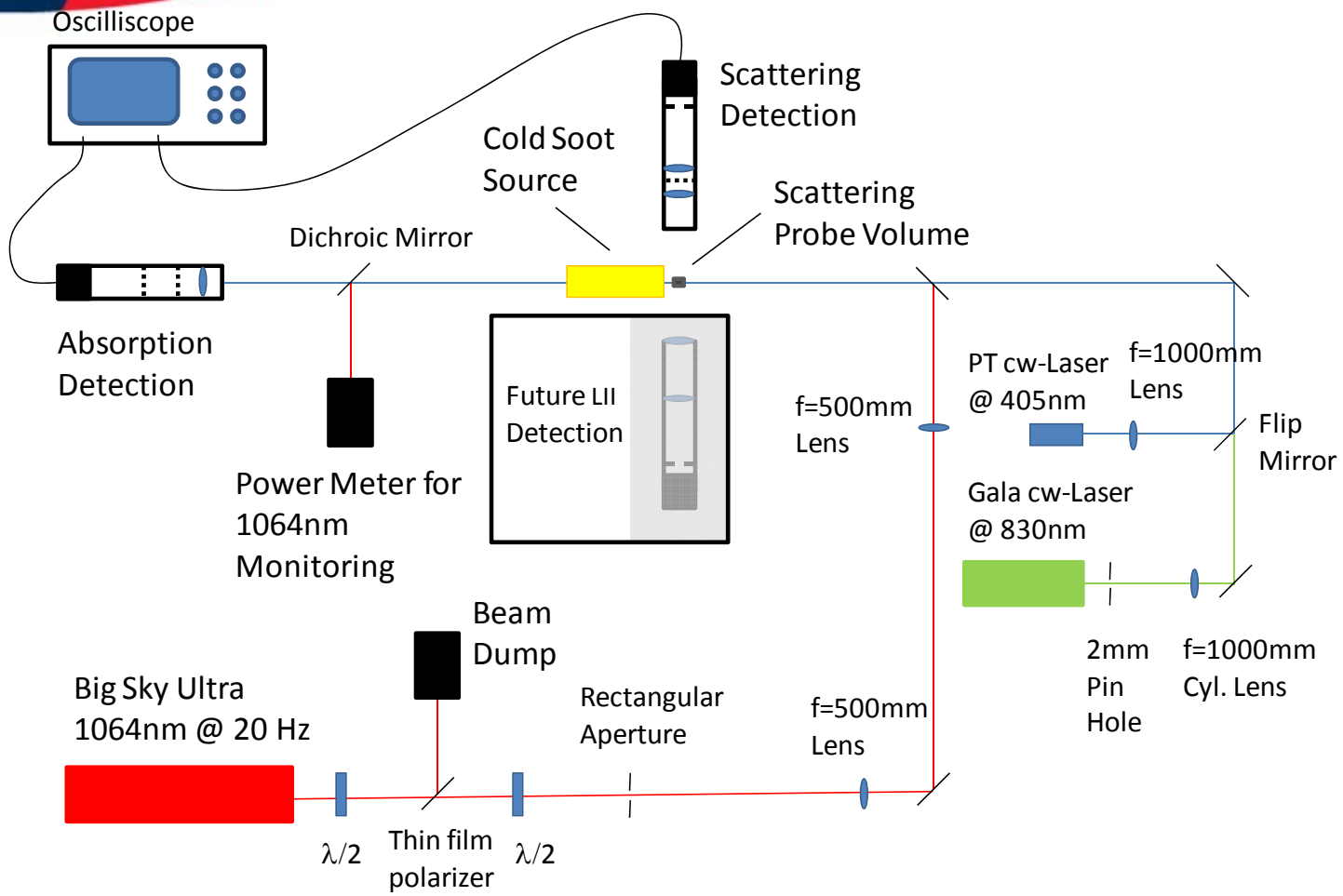
Apparatus - Optics



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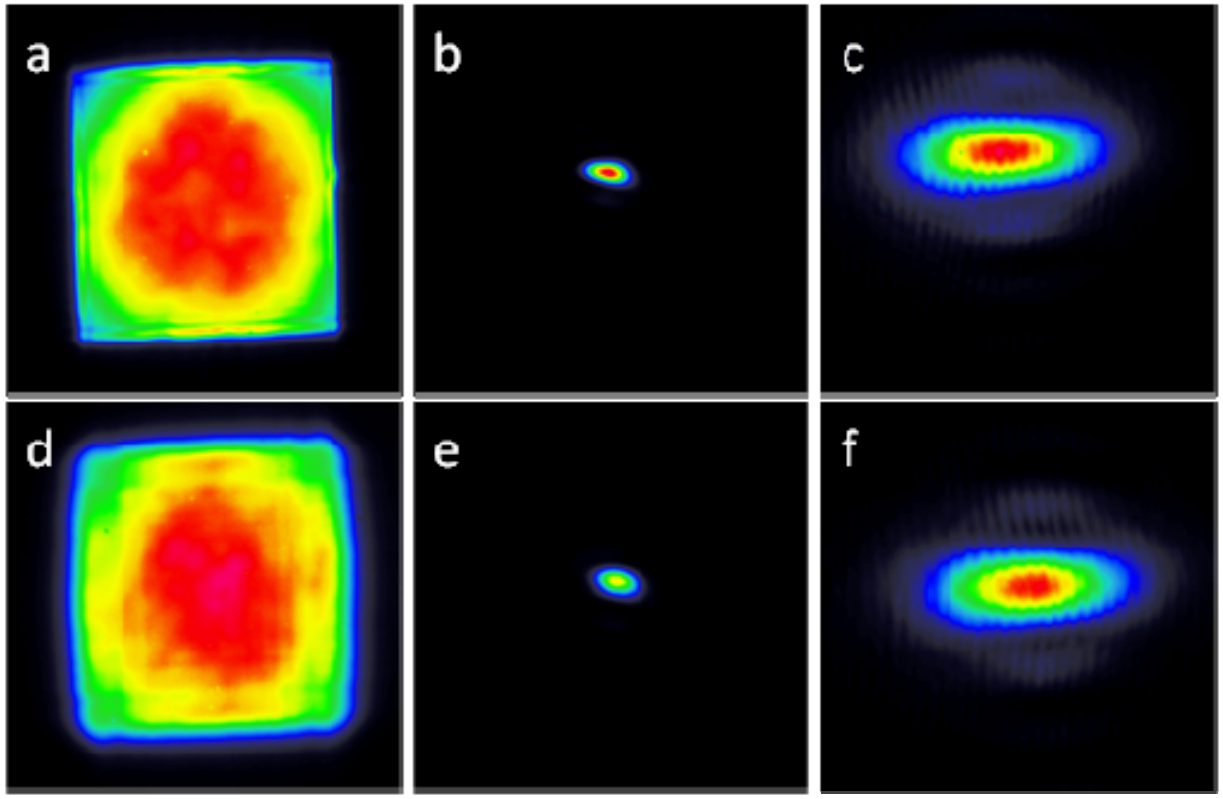
Laser beam profiles

Tube Entrance

Tube Exit



1064 nm 405 nm 830 nm

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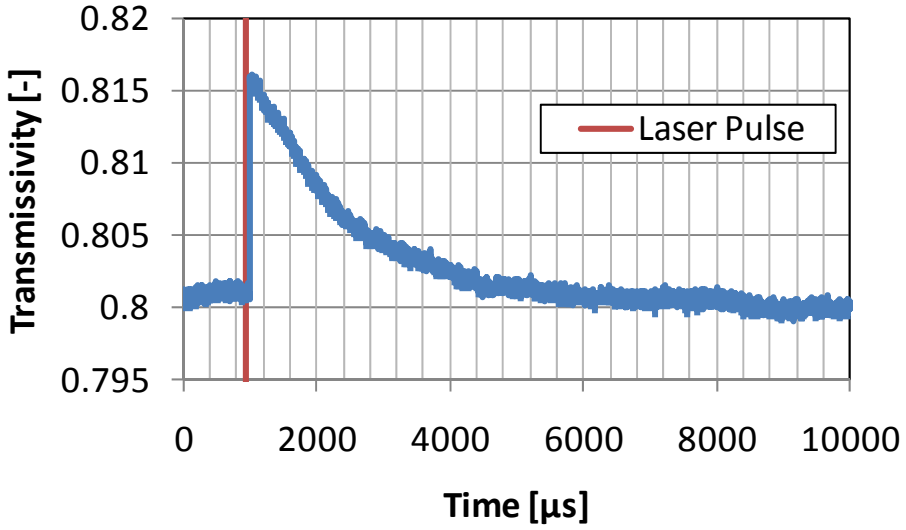
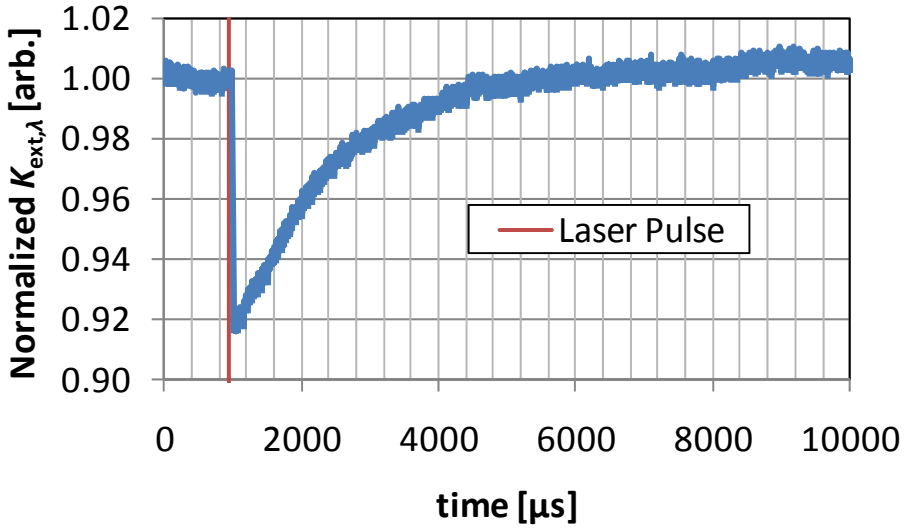
830 nm LOSA
Fluence = 1.4 mJ/mm²

Transmissivity



Normalized Extinction Coefficient



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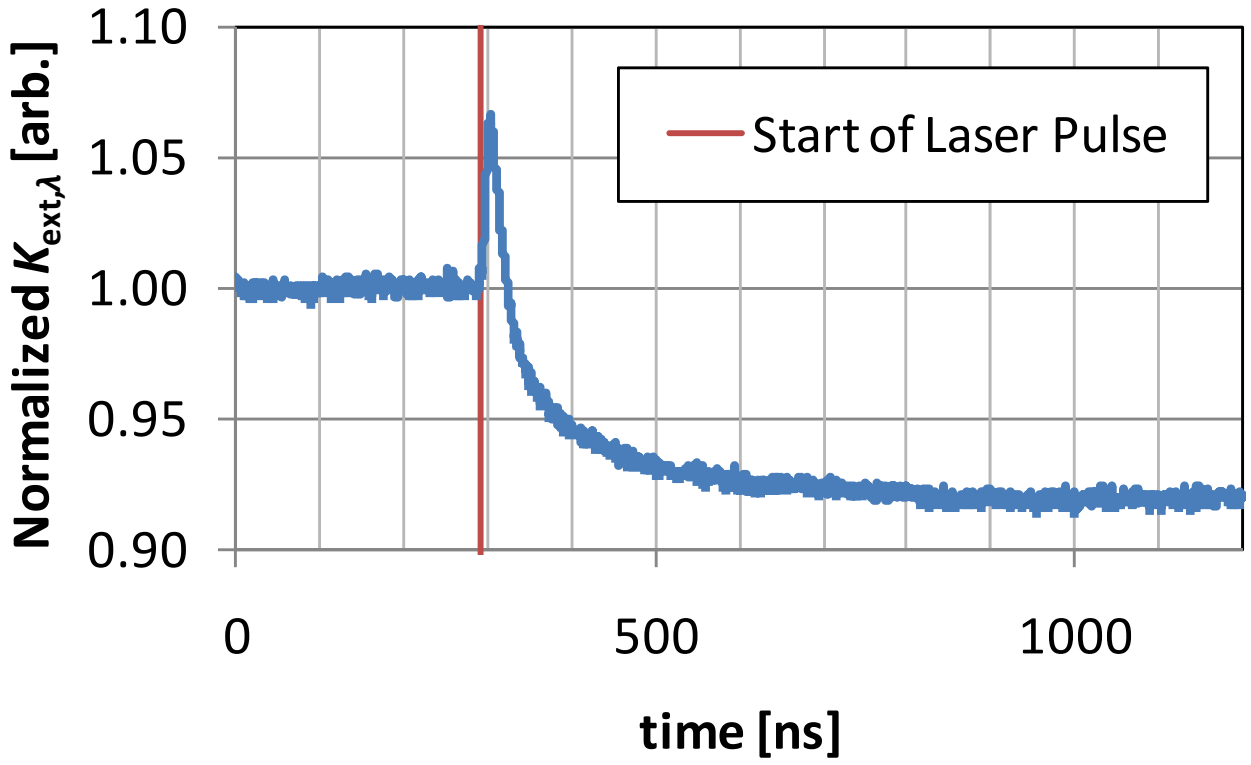
830 nm extinction coefficient



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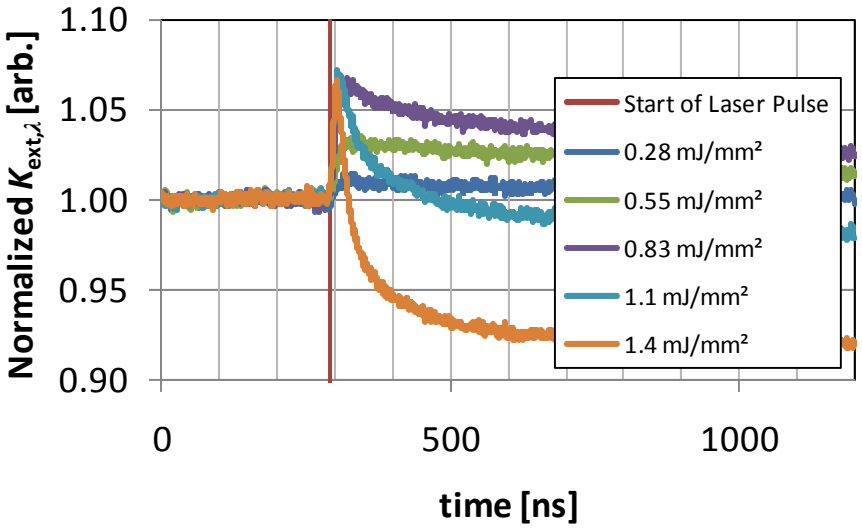
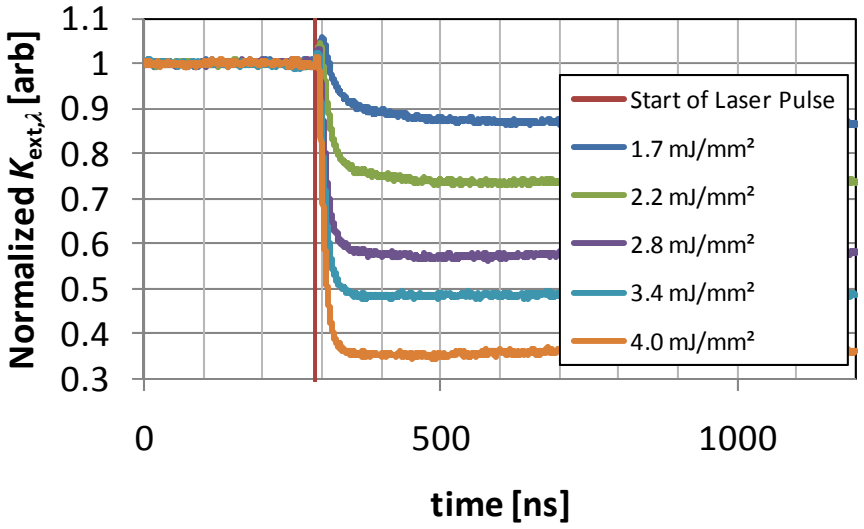
830 nm extinction coefficient



Low fluence range



High fluence range

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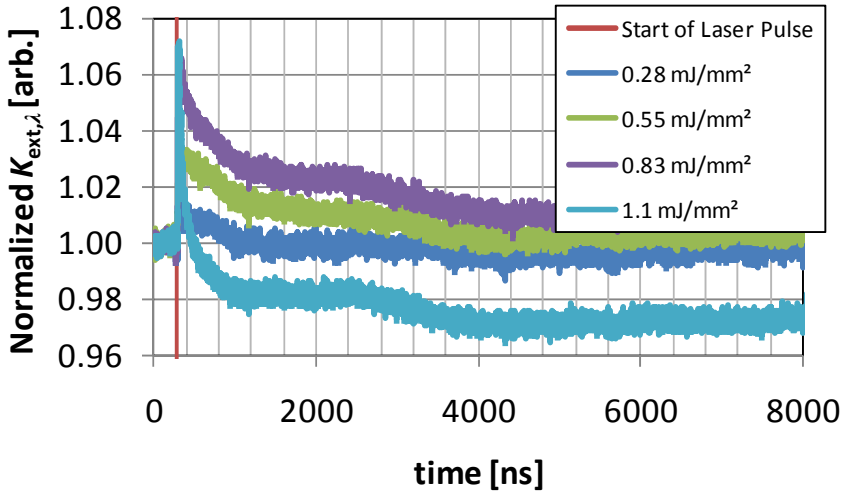
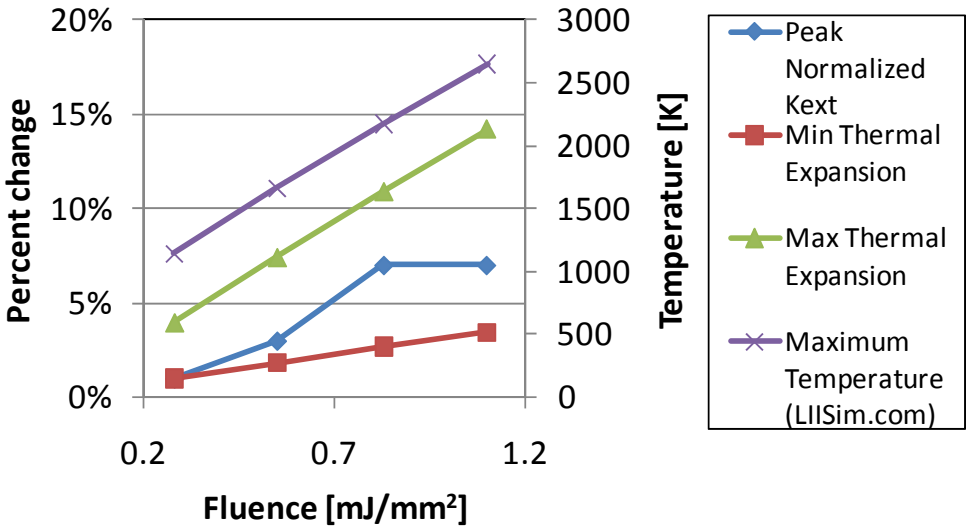
830 nm extinction coefficient

Change in Extinction Coefficient



Relation to Thermal Expansion



- Increase of 830 nm extinction coefficient *could* be explained by thermal expansion of the particles

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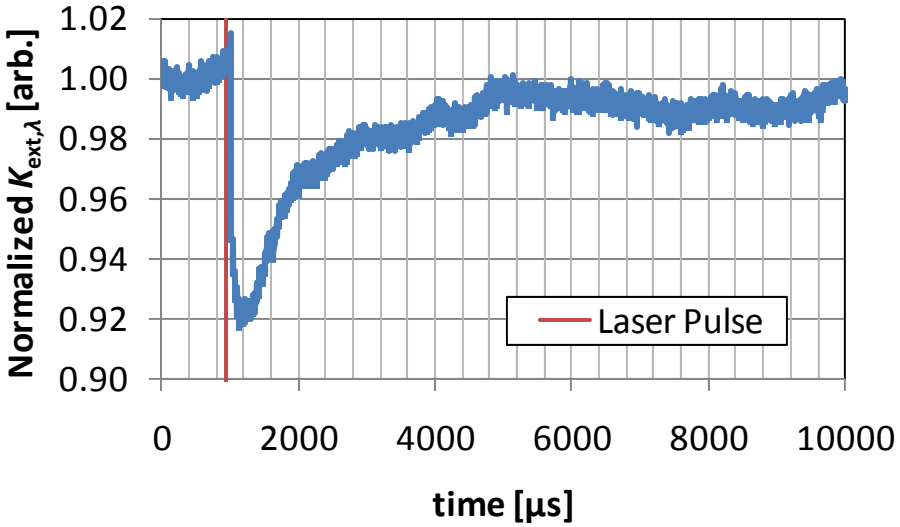
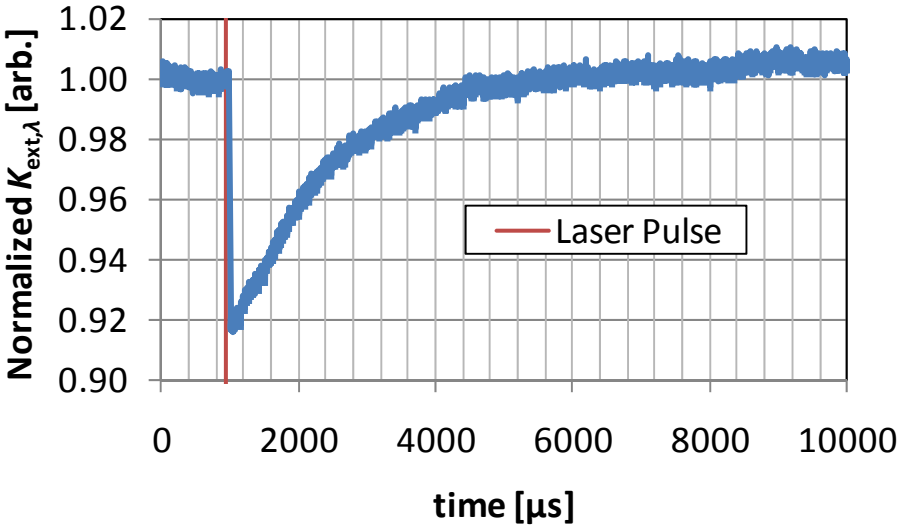
405 nm versus 830 nm extinction coefficients

405 nm



830 nm



- Similar magnitude of variation
- Slower initial drop (30 µs verses 30 ns!)

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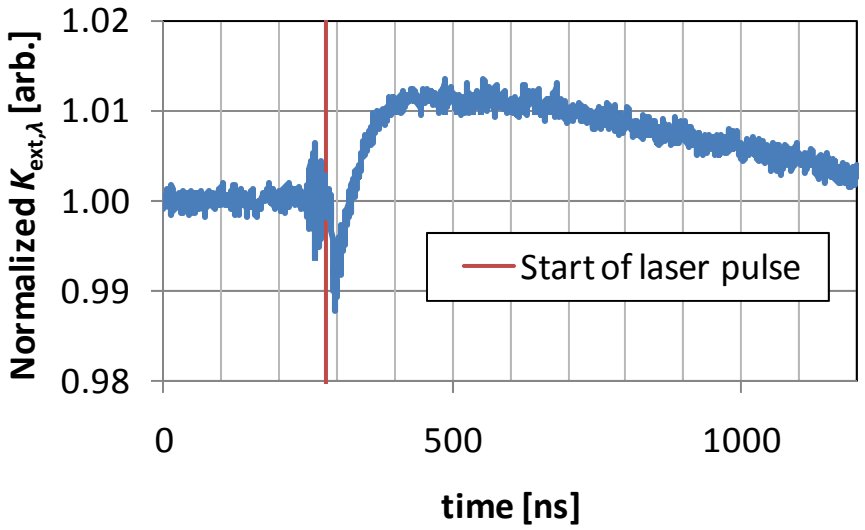
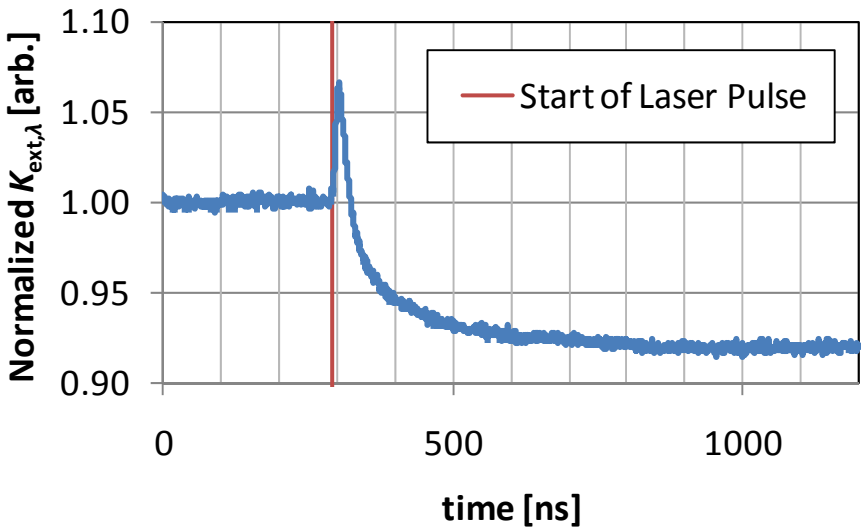
405 nm versus 830 nm extinction coefficients

405 nm



830 nm



- Opposite trends!
- Possible indication of desorption of PAH/fragments from soot
  - Desorbed material could still attenuate light at 405 nm

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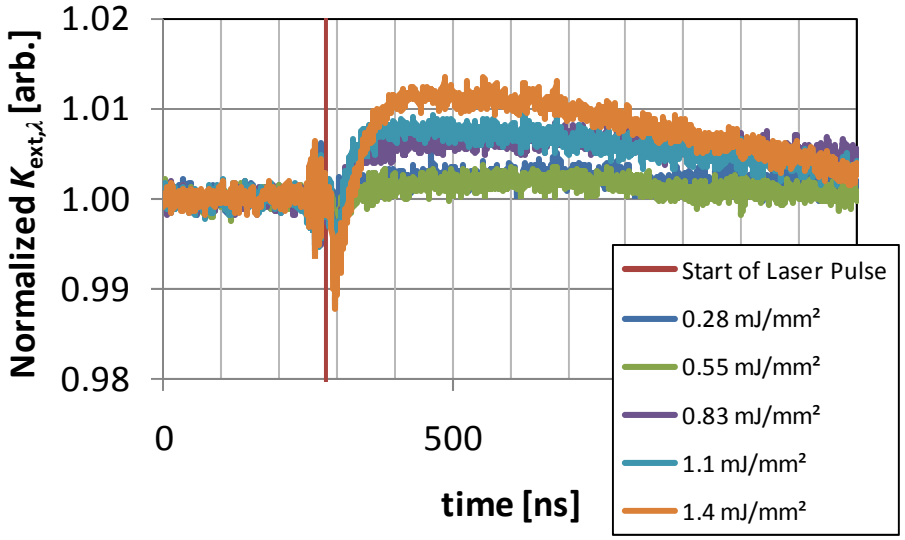
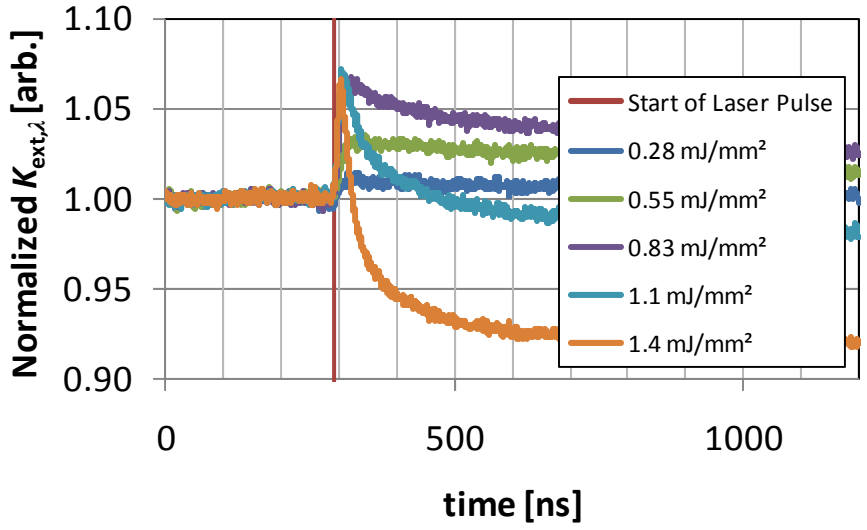
405 nm versus 830 nm extinction coefficients

405 nm



830 nm



- $K_{ext,405}$ initially decreases at all fluences
- Again, opposite to 830 nm data
- Small temperature increase needed to desorb PAH/fragment?

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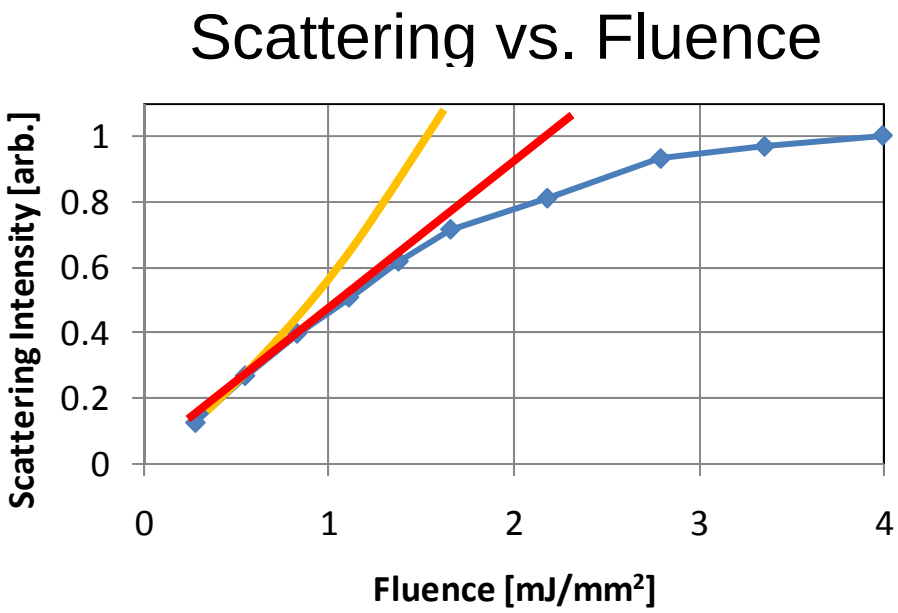
1064 nm elastic light scattering



- Scattering efficiency decreases with increasing fluence
  - Scattering does not appear to scale with $d_p(T)^6$

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Conclusions

- measurements are not sufficient to entirely resolve the original questions, but they do offer several important insights:
  - enhanced light absorption is observed and the magnitude could be explained by thermal expansion of soot particles
  - the onset of soot sublimation is as low as 1.0 mJ/mm^2
  - 405 nm extinction suggests desorption of a surface coating
  - ejected material absorbs and possible emits at 405 nm
  - 1064 nm light scattering efficiency does not increase with particle size increase
    - likely proportional to the amount of material in the particle (i.e mass) rather than the volume

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Conclusions

- implications for LII
  - small increase of $K_{abs,\lambda}$ @ near infra-red wavelengths can and should be accounted for in LII model
  - change of $K_{abs,\lambda}$ @ ultra-violet wavelengths difficult to interpret and predict
    - some evidence of material desorption, but does desorbed material emit and for how long?

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Future Work/ Acknowledgements

- Confirmation of current measurements
- LII measurements

- Acknowledgements:
  - Helmholtz/NRC collaboration
  - Our partners at DLR Stuttgart

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Science
at work for
Canada

National Research Council Canada
Conseil national de recherches Canada

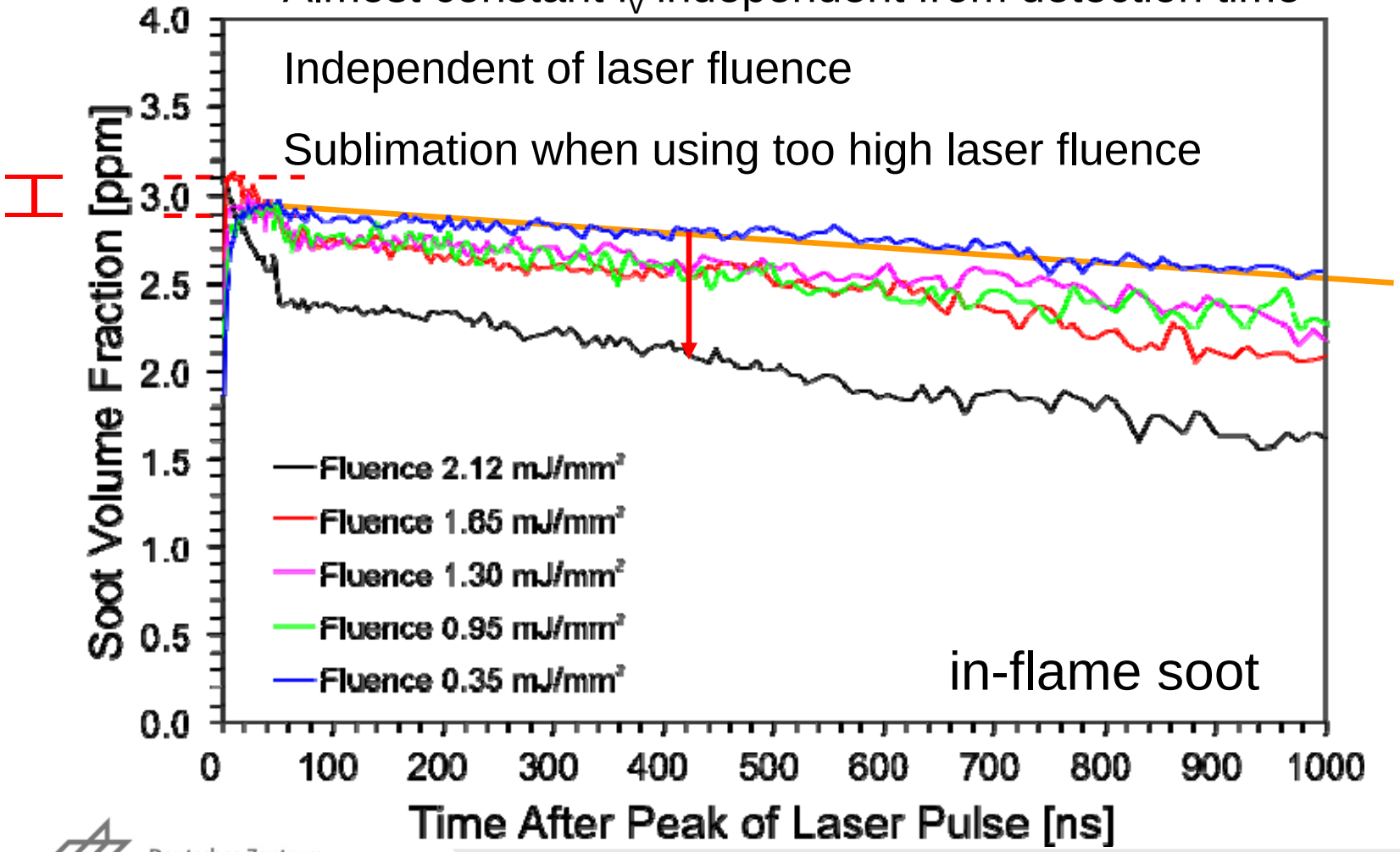
Canada

Motivation - expected

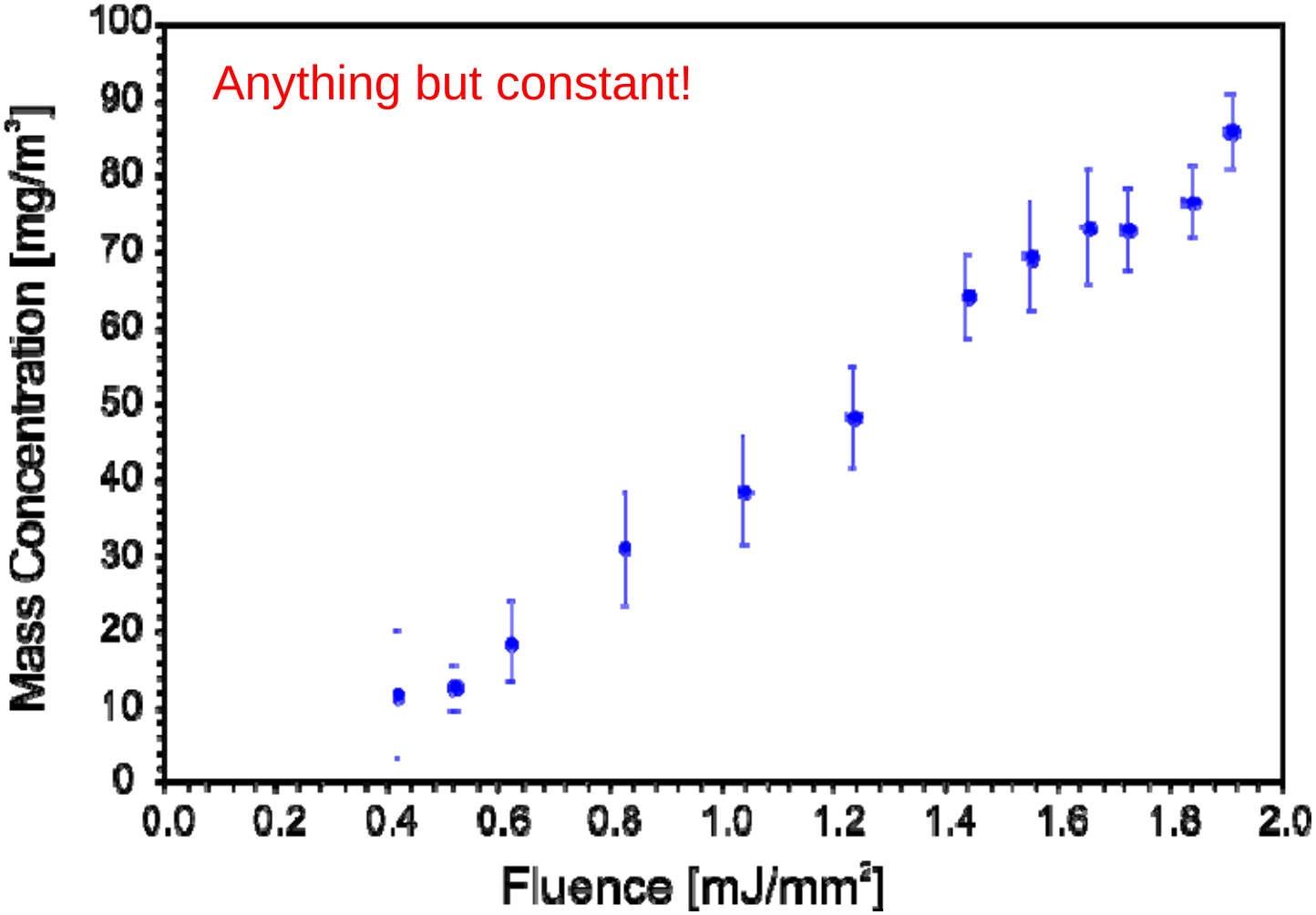
Almost constant f_v independent from detection time

Independent of laser fluence

Sublimation when using too high laser fluence



Motivation – found for cold (after flame) soot …



Mass Concentration of Nonvolatile Nanoparticle Emissions: Comparison of Autocompensating Laser-Induced Incandescence (AC-LII) to Other Techniques

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A number of LII instruments were compared against a range of other instruments and techniques for determining the mass concentration of nonvolatile particulate matter (nvPM). LII was found to correlate well with most methods that claim to be specific to nvPM, but there was variability in the systematic uncertainty between the techniques. Applications included a laboratory soot generator, a gas flare, atmospheric black carbon, a diesel engine, and gas turbine emissions.

Introduction

Laser-based measuring techniques are important tools for understanding soot formation and oxidation in flames and for the quantification and characterization of particulate emissions from energy generation, industrial, and mobile sources. The drive to lower soot concentrations is produced by evermore stringent particulate matter (PM) emissions regulations. These regulations are in response to health and environmental concerns about air quality and nanoparticles in the atmosphere.

As a result, there is a need to measure black carbon levels in the atmosphere at microgram per cubic metre or lower mass concentrations. At the same time, emission standards for Diesel particulate matter (PM) are being lowered dramatically, resulting in the adoption of Diesel particulate filters (DPFs) by manufacturers, and there is a need to measure solid carbon levels in the exhaust and in dilution tunnels at microgram per cubic metre or lower mass concentrations.

Advances in optical diagnostics of nanoparticles have led to the recent emergence of techniques such as laser-induced incandescence to measure the concentration and size of nonvolatile aggregated nanoparticles emitted into the atmosphere during the production of energy through fossil fuel combustion. There has been significant progress in the understanding of the physics and chemistry related to the nanoscale processes that occur as a result of the rapid heating and cooling of soot nanoparticles due to laser irradiation during the laser-induced incandescence (LII) process for measuring soot nanoparticles (Schulz *et al*., 2006).

Laser-induced incandescence (LII) offers many advantages and unique capabilities over existing measurement technologies, including specificity to measuring refractory carbon (RC), the primary constituent of nonvolatile particulate matter (nvPM) emitted from combustion. LII has been identified as a leading candidate for the measurement of mass concentration of nvPM from aviation engines (SAE, 2010). A detailed comparison of LII instruments against existing measurement technologies was required to demonstrate its capabilities for potential standardized measurements of nvPM. Measurement comparisons were performed and evaluated.

Experimental

The Artium Technologies LII 200 and LII 300 (Figure 1) instruments are commercial instruments based upon the autocompensating laser-induced incandescence (AC-LII) technique developed at the National Research Council Canada (Snelling *et al*., 2005; Smallwood, 2009). While most comparisons are performed with these commercial instruments, suitability for ambient measurements of atmospheric black carbon required application of a high sensitivity laser-induced incandescence (HS-LII) system (Smallwood, 2009).

The HS-LII system consisted of a Big Sky CFR 200 multimode pulsed Nd:YAG laser, operating with 200 mJ/pulse at 20 Hz and 1064 nm as the excitation source. The laser was equipped with an electro-optic q-switch to produce a laser light pulse with a smooth profile of 7 ns FWHM (full-width at half of maximum) duration. A half-wave plate (to rotate the plane of polarization) in combination with a thin film polarizer (angle-tuned to transmit horizontally polarized radiation) was used to adjust the laser energy as required. A second half-wave plate was used to return the plane of polarization of the transmitted laser light beam to vertical. To optimize the uniformity of the laser beam at the probe volume, the laser beam was expanded into a vertical light sheet and a rectangular aperture was placed in the beam prior to the probe volume. Low fluence LII, 0.15 J/cm^2 was typically employed to limit the peak temperatures to <4000 K, ensuring that negligible soot sublimation occurred.

The instruments were calibrated using an integrating sphere with a NIST-traceable spectrometer to monitor its output. This determined the absolute spectral radiance sensitivity of the LII systems.

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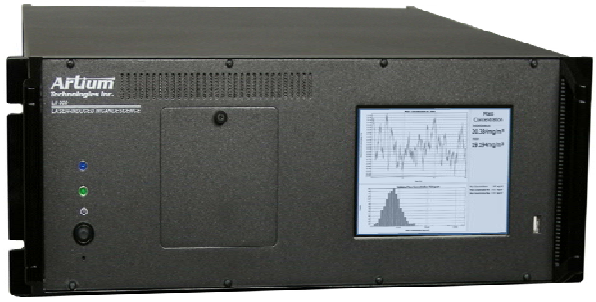

Figure 1 Artium Technologies LII 300 instrument.

These systems were applied to measure the mass concentration of particulates from a Mini-CAST soot generator (LII 200), a turbulent gas flare (LII 200), atmospheric black carbon (HS-LII), Diesel exhaust (LII 300), and gas turbine emissions (LII 300). All instruments and techniques applied in each comparison were operated simultaneously so that any variations in concentration were accounted for.

Results

The LII 200 instrument was applied to measure the mass concentration of soot emitted by a mini-CAST soot generator. The concentration of soot that was measured was varied by varying the flame conditions in the soot generator and by diluting the output of the soot generator. The comparison was to a Sunset Laboratories EC/OC analyzer, a thermo-optical technique compatible with the NIOSH 5040 standard for measuring the elemental carbon (EC and organic carbon (OC) mass concentrations in particulate matter.

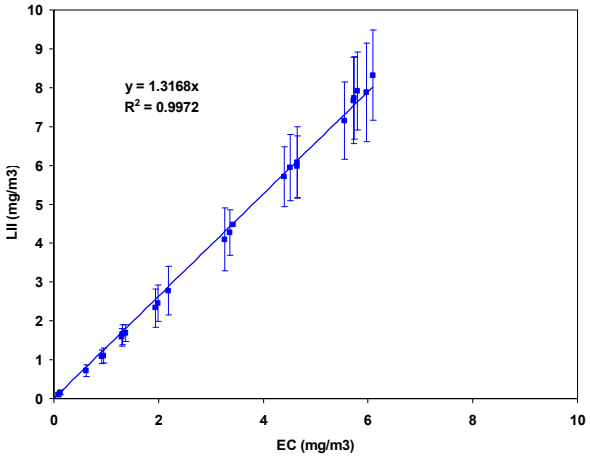

Figure 2 LII 200 measurements of soot concentration from miniCAST soot generator compared to elemental carbon concentration determined by the NIOSH 5040 method.

The LII 200 results correlated extremely well with the NIOSH 5040 determination of EC, as shown in Figure 2, with a correlation coefficient of 0.997 holding over two orders of magnitude variation in concentration. There was a discrepancy in mass concentration, with the LII values about 1.3 times greater than those determined by NIOSH 5040. This could be due to a calibration issue with one or the other instrument, with both instruments, or due to the fact that EC is not the same as RC.

The soot emissions produced by a turbulent gas flare with a variety of fuels representing typical mixtures found in the oil and gas industry were measured with the LII 200 and by the gravimetric filter method. The results (Figure 3) demonstrated a weaker correlation and the LII results were less than the gravimetric results by a factor of 0.8. The weaker correlation may be due to the range of fuels studied, as each fuel may produce a different level of volatile particulates, which are measured by the gravimetric method but not detected by the LII 200. These volatile particles may also explain the fact that the LII results were lower than the gravimetric results.

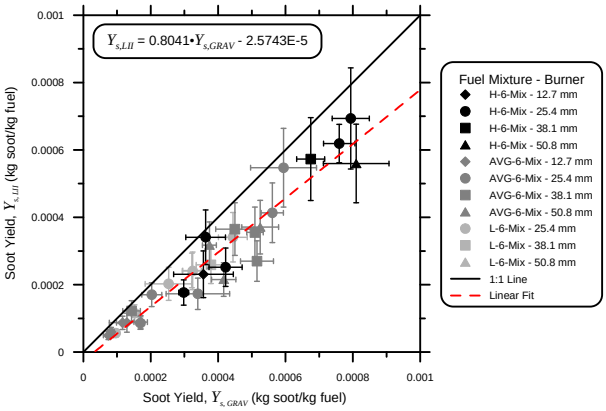

Figure 3 Measurements of emissions from a soot flare comparing the LII 200 and gravimetric results.

The photoacoustic instrument was studied as it claims to measure black carbon directly, and thus should perform similarly to the LII technique. A study of emissions from the hot section of a gas turbine where the emissions were expected to be predominantly nvPM resulted in a high correlation of 0.991 between the LII 300 and photoacoustic instruments, and almost identical values (a slope of nearly 1.0), as shown in Figure 4. This level of agreement was likely due to the absence of volatile particles and the low uncertainty associated with the calibration of the instruments.

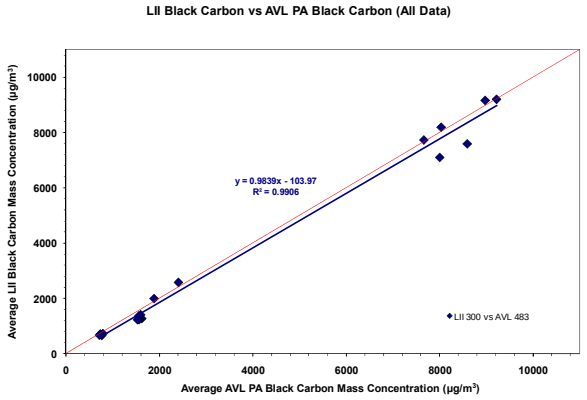

Figure 4 Measurements of emissions from a gas turbine comparing the LII 200 and photoacoustic instruments.

The same instruments were applied to the exhaust of a modern diesel engine operating without a diesel particulate filter, and compared to the concentration of total particulate matter as determined by the gravimetric filter method. As shown in Figure 5, both the LII 300 and the photoacoustic instrument demonstrate results significantly lower than the total particulate matter determined gravimetrically. Both have a correlation well above 0.9, but are only a factor of about 0.5 the value of the gravimetric data. This is likely due to the significant presence of non-refractory carbon species in the particulates, including volatiles, sulphates, nitrates, and ash.

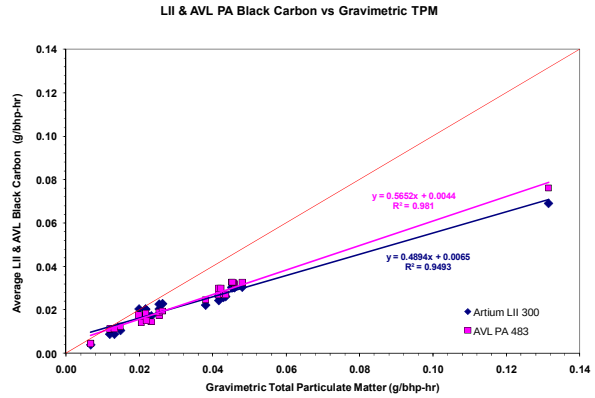

Figure 5 Measurements of emissions from a diesel engine comparing the LII 200 and photoacoustic instruments against gravimetric results.

In a series of experiments studying ambient levels of atmospheric black carbon, HS-LII, photoacoustic, and aerosol mass spectrometer (AMS) instruments were simultaneously applied in a range or urban and suburban environments. The AMS was able to determine the mass loading of volatile particulate matter, which was used to assess the mass loading of volatile coatings on the black carbon particulate matter. As shown in Figure 6, as the mass loading of the volatile coating increased, the photoacoustic instrument demonstrated a significant change in its response, whereas the HS-LII showed no significant effect. While these coating levels were higher than would be normally expected when monitoring emissions from combustion systems, the results indicate that LII instruments were not affected by the presence of volatiles whereas the photoacoustic instrument was significantly affected.

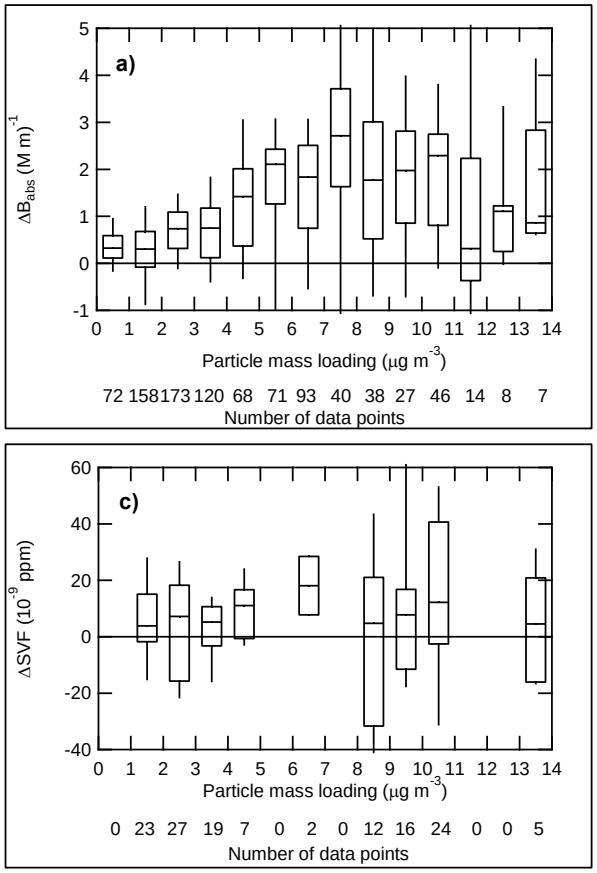

Figure 6 Measurements of atmospheric black carbon comparing the HS-LII and photoacoustic instruments. The variations of (a) the particle light absorption (photoacoustic) and (c) the soot volume fraction (HS-LII) as a function of particle volatile coating mass are shown (Chan et al., 2010).

Summary

A range of LII instruments were demonstrated to be highly correlated, repeatable, precise, selective, and linear with respect to some other particle measurement techniques. Real-time measurements and high sensitivity also achievable.

However, the LII instruments have shown differences in the absolute concentration when compared to some other methods. Comparisons to total particulate matter are difficult due to the presence of volatiles and other non-carbon substances, and to large particles if a $PM_{1.0}$ cutoff cyclone is not used.

PM mass measurements are highly sensitive to sampling conditions, including dilution, and instrument operation. Care must be exercised when comparing measurement techniques, as the principles of operation and the measurands vary greatly.

Acknowledgements

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