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Determining the Mean Aggregate Size of Soot Particles with the Combination of Light Scattering and Two-Colour Time-Resolved LII

Sub-Task 3.4S

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Motivation/Objective

- Motivation
  - details of the morphology of soot/black carbon aggregates are necessary to assess the health and environmental impacts of these nanoparticles

- Objective
  - extend the capabilities of LII to include the determination of the mean number of primary particles per aggregate

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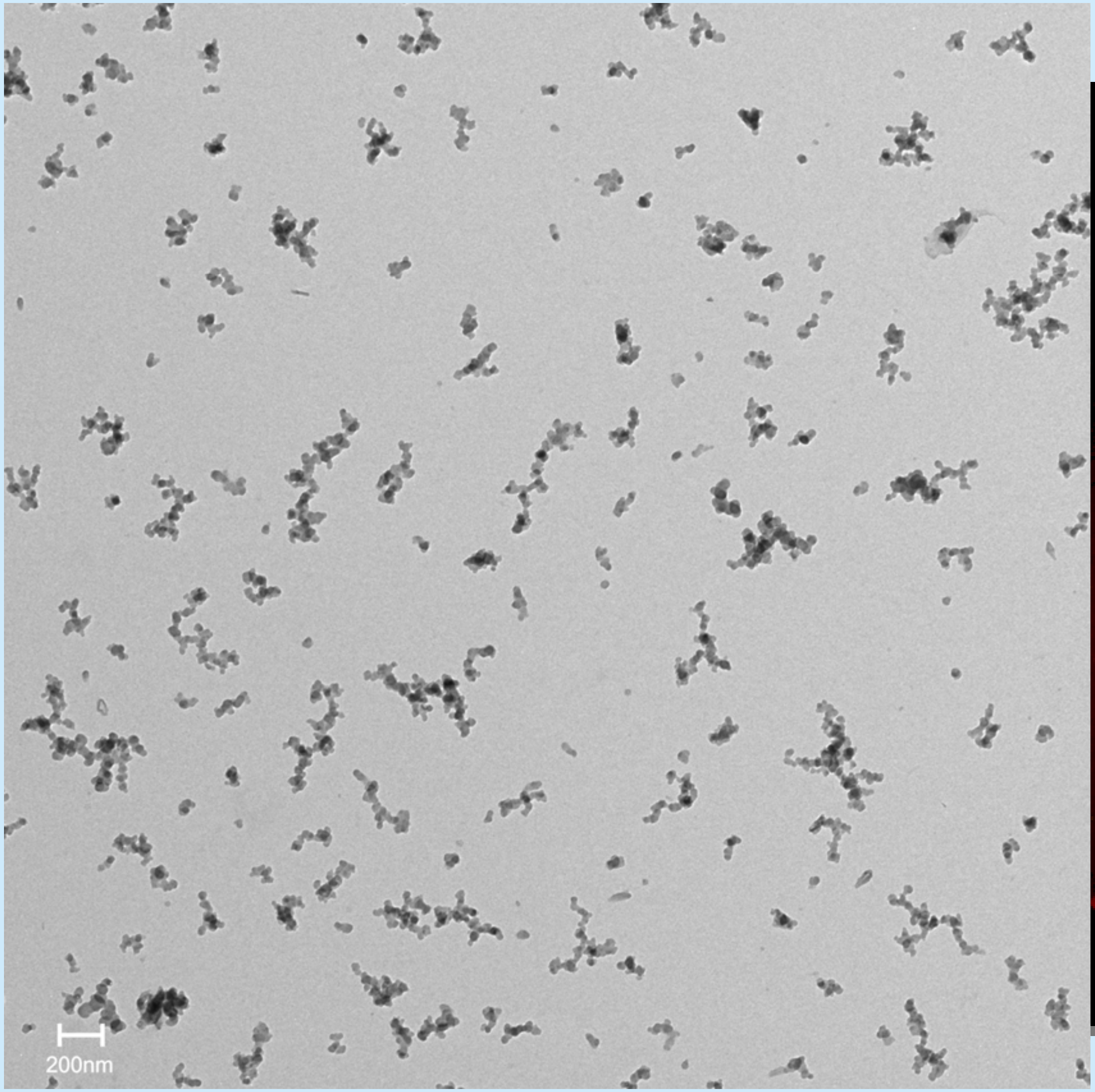
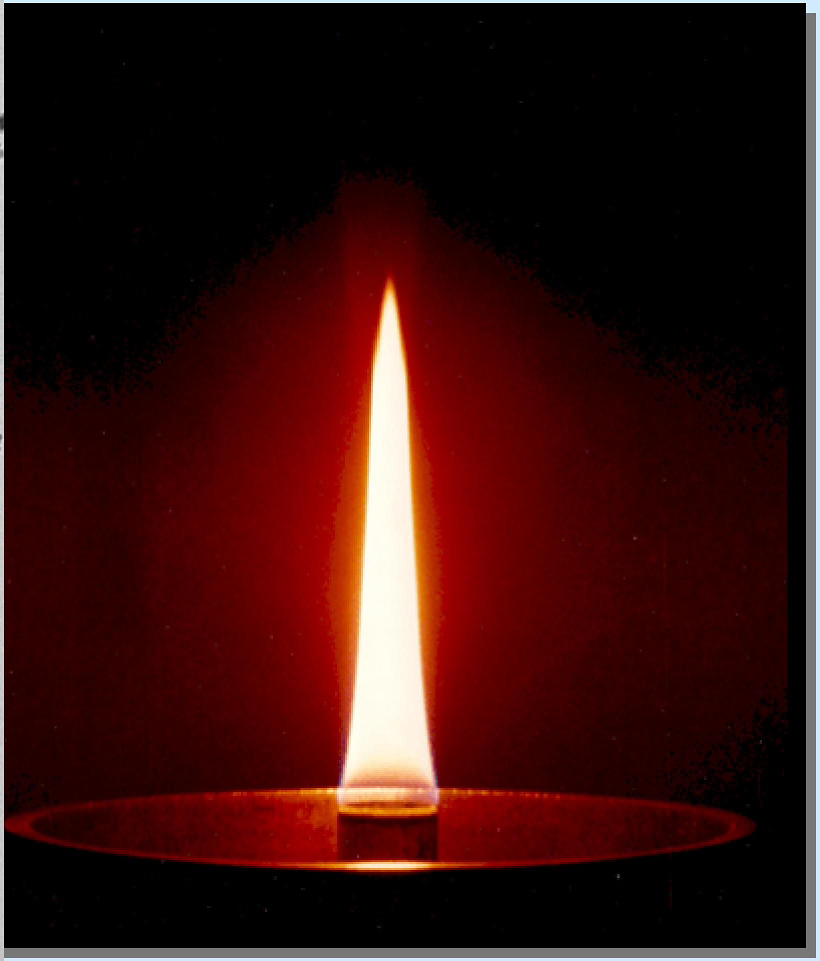
Background

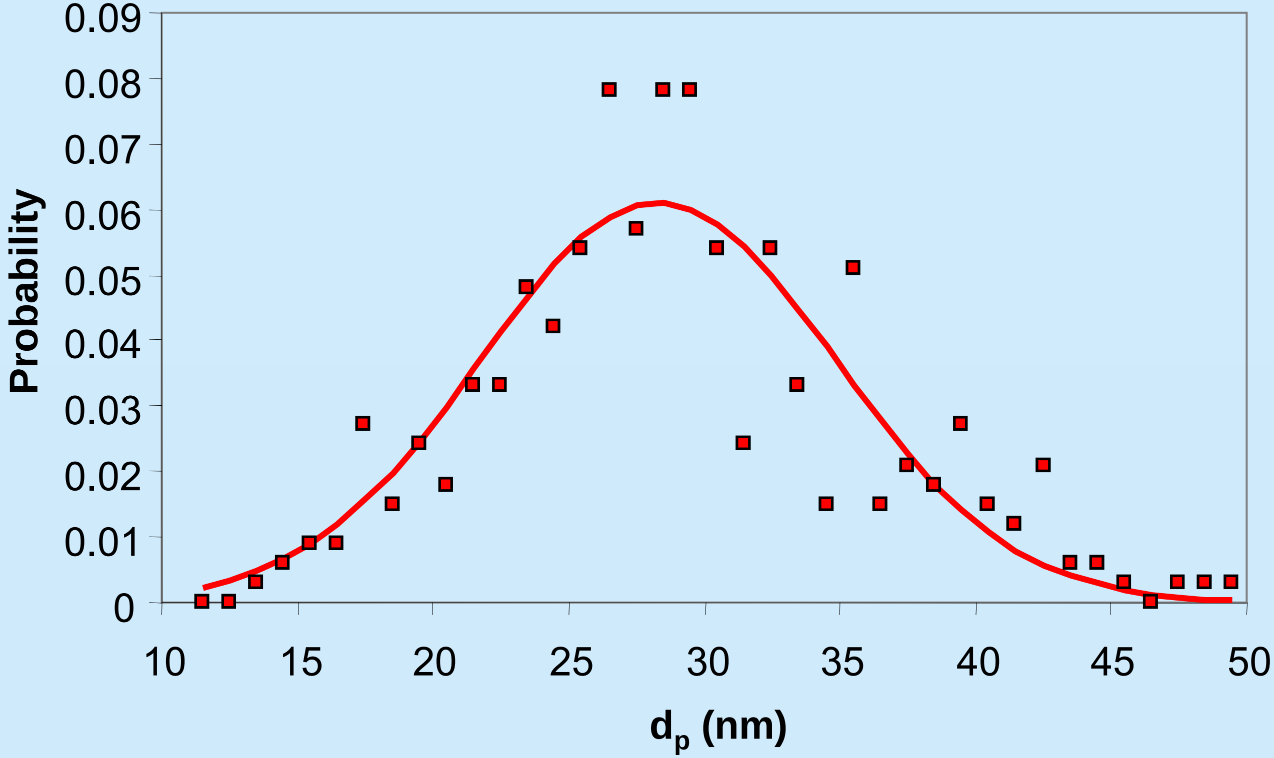
- laser-induced incandescence (LII) has become a well established technique for measuring soot concentration and primary particle diameter
- soot aggregate size (number of primary particles per aggregate) distributions are described by a lognormal function whose distribution width is largely independent of the soot source and the (geometric) mean aggregate size
- due to the relative insensitivity of the distribution width it is possible to determine mean aggregate size from a combination of absolute LII signals and near forward laser light scattering

TEM image of soot particles sampled from a flame





Primary Particle Size Distribution



- 385 measurements of primary soot particles
- arithmetic mean diameter: D_{10} = 29.2 nm
- normal distribution fit: d_m = 28.3nm and σ_d = 6.5nm

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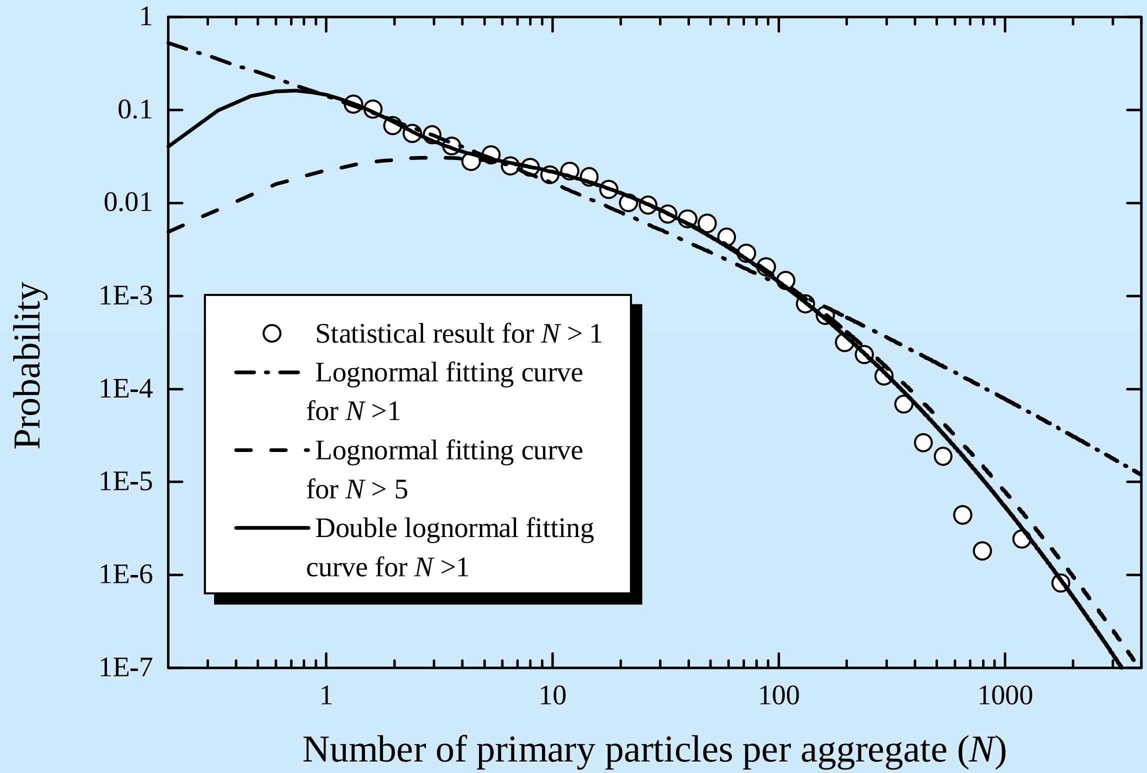
Aggregate Size Distribution

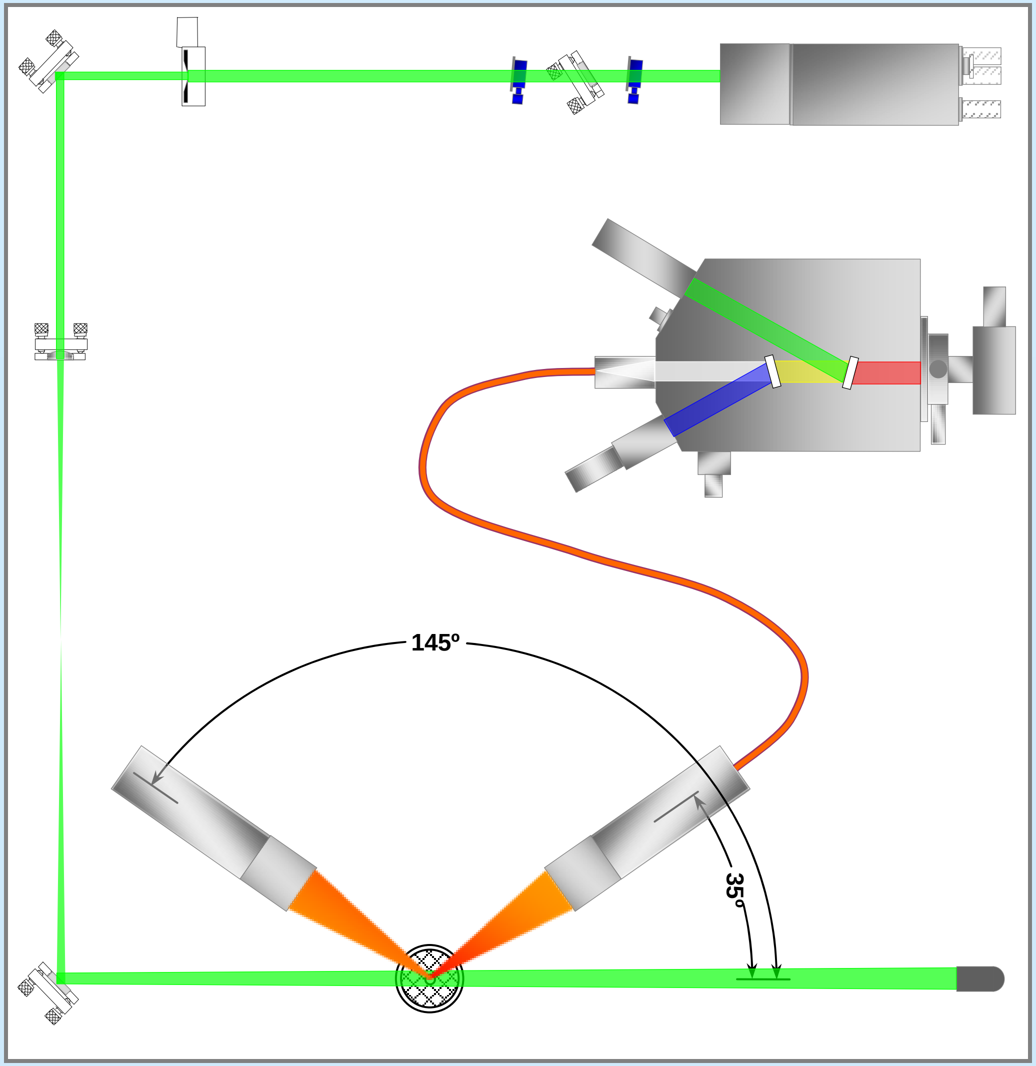


- 3400 aggregates measured
- for a lower limit of N_p>5: N_g=23.2, σ_{2g}=4.15

Approach

- modification of a typical 2-color time-resolved LII system allows simultaneous time-resolved measurement of 2-color LII and single-angle absolute scattering intensity from a 532 nm LII excitation source
- a single measurement can result in estimates of soot volume fraction, the primary particle diameter and the geometric mean aggregate size
- the mean aggregates sizes derived with this method depend on a knowledge of the ratio of the soot absorption and scattering functions
- this *in situ* technique is applied to soot in a laminar diffusion flame
- an enhanced technique that requires no knowledge of the absorption or scattering function values, based on the ratio of forward to backward scattering, is also evaluated

AC-LII / Scattering Apparatus



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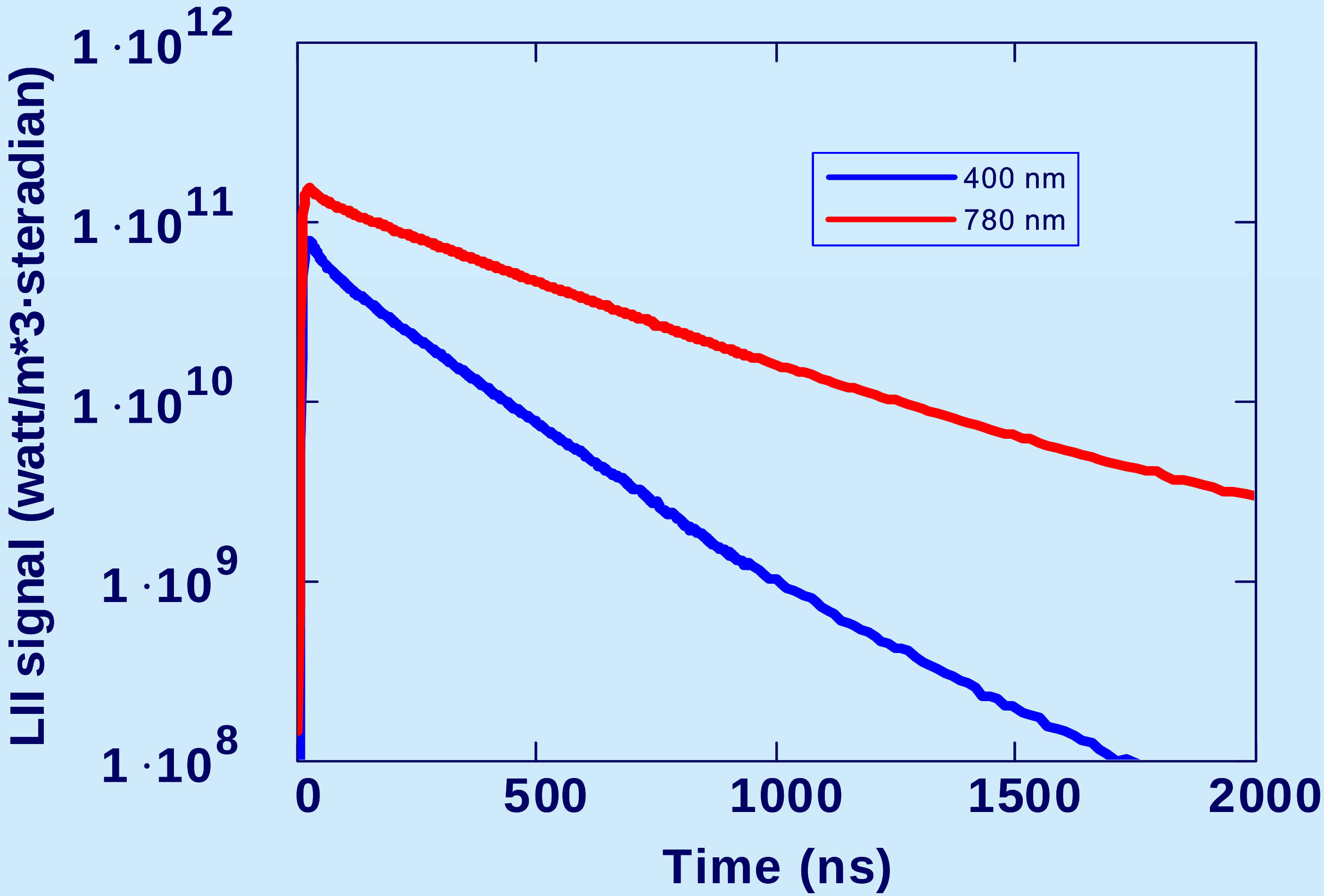
Soot volume fraction from 2-colour LII

$$f_v = \frac{V_{EXP}}{\eta\, w_b G_{EXP} \dfrac{12\pi c^2 h}{\lambda_C{}^6} E\left(m_{\lambda_C}\right)\left[e^{\frac{hc}{k\lambda_C T_{pe}}} - 1\right]^{-1}}$$

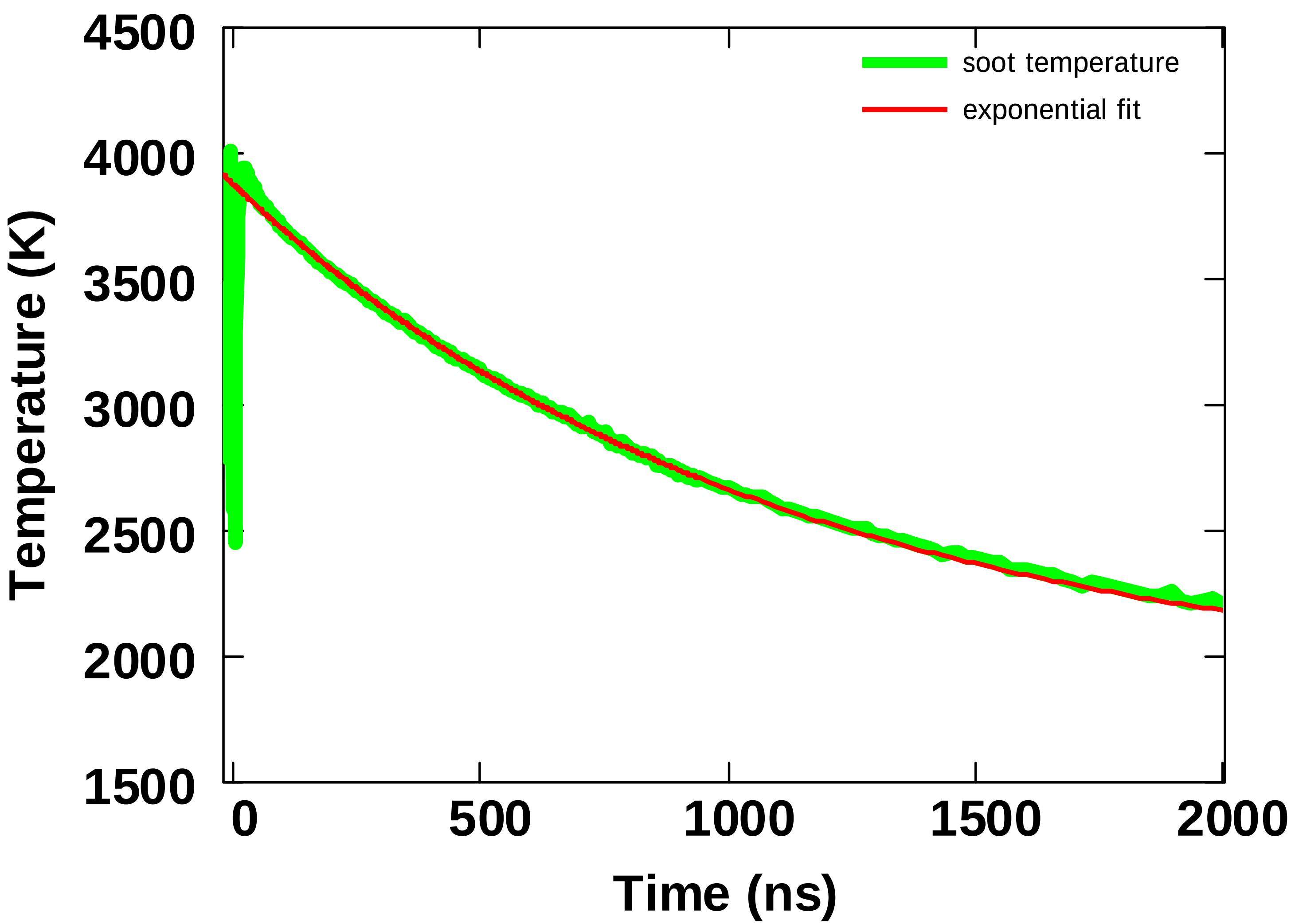
η	calibration factor	T_{pe}	equivalent particle temperature
G	amplifier gain	w_e	equivalent laser width
V	potential	m	refractive index
λ_C	centre wavelength	E	absorption function

- the soot volume fraction (f_v) derived from LII (or absorption) is inversely proportional to the value of $E(m)$ assumed
- the property determined by LII is the product of soot volume fraction and the absorption function

Absolute LII Signals



Real-time Temperature



Soot scattering theory – I

- based on Rayleigh-Debye-Gans Polydisperse Fractal Aggregate (RDG-PFA) theory
- aggregate differential scattering cross section:

$$\sigma_{ag} = N^2 \frac{\pi^4 d_p^6 F(m)}{4 \lambda^4} S(q, R_g)$$

N	number of primary particles
d_p	primary particle diameter
$S(q,R_g)$	structure factor

- scattering vector, $q(\theta)$:

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

- fractal radius of gyration, R_g:

$$R_g = \left(\frac{N}{k_f}\right)^{\frac{1}{D_f}} d_p$$

Soot scattering theory – II

- structure factor is calculated numerically using the confluent hypergeometric approach of Sorensen, which assumes a Gaussian fractal cut-off
- for a distribution of aggregates the scattering cross section must be integrated over the appropriate distribution function
- lognormal distribution:

$$P_{lognorm}\left(N, N_g, \sigma_g\right) = \frac{\exp\left[-\left[\left(\frac{\ln(N)-\ln(N_g)}{\sqrt{2}\ln(\sigma_g)}\right)^2\right]\right]}{N\ln(\sigma_g)\sqrt{2\pi}}$$

N_g geometric mean aggregate size
σ_g distribution width

- to derive N_g from the ratio of soot scattering to LII intensity and the known soot scattering and absorption functions we must assume a distribution width σ_g

Soot scattering theory – III

- Sorensen has shown that a self preserving or scaling distribution gives a more accurate description of the higher moments that describe scattering than does a lognormal distribution
- a self preserving distribution is theoretically predicted from solving the aggregate coagulation equations over a wide range of conditions
- an aggregating system develops a self preserving scaling distribution.
- lognormal distribution moments with a width ~2.5 are in best agreement with the scaling distribution up to the 3rd moment
- experimental evidence of flame soot σ_g ~2.6, used for subsequent analysis

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Volumetric scattering coefficient

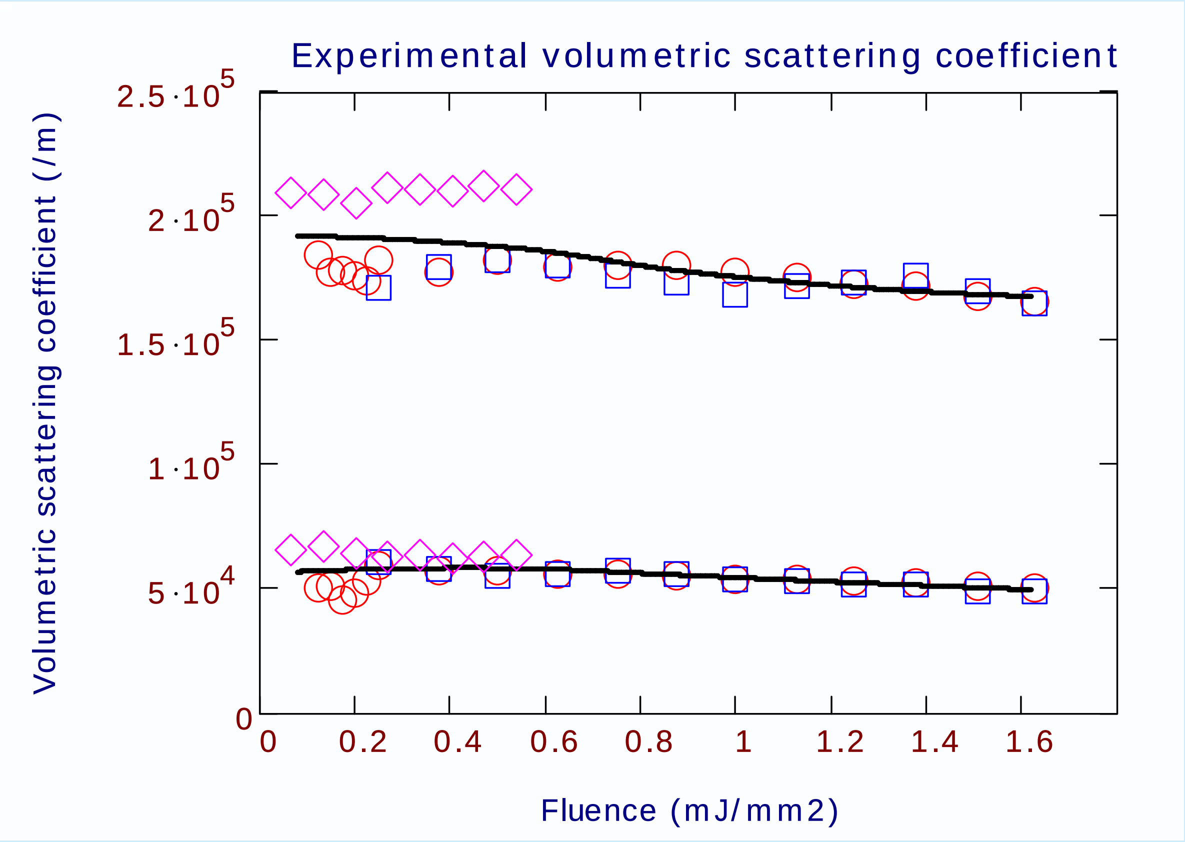
$$C_{vol} = N_{ag}\sigma_{ag} = \int_1^\infty P_{lognorm}\left(N, N_g, \sigma_g\right) N^2 \frac{\pi^4 d_p^6 F\left(m_{532}\right)}{4\lambda^4} S\left(q, R_g\right) dN \; \frac{f_v\, 10^{-6}}{\frac{\pi d_p^3}{6} N_g \exp\left(0.5 \ln\left(\sigma_g\right)^2\right)}$$

- the soot volume fraction from LII is inversely proportional to the value of *E*(*m*) assumed at the LII wavelengths
- this allows substitution of the requirement to know the relative value of *E*(*m*) from 400 to 780 nm and the ratio *F*(*m*)/*E*(*m*) at 532 nm for a knowledge of the absolute values of the coefficients

$$C_{vol} = \int_1^\infty P_{lognorm}\left(N, N_g, \sigma_g\right) N^2 \frac{\pi^4 d_p^6 F\left(m_{532}\right)}{4\lambda^4 E\left(m_{532}\right)} S\left(q, R_g\right) dN \; \frac{f_v\, 10^{-6} E\left(m_{532}\right)}{\frac{\pi d_p^3}{6} N_g \exp\left(0.5 \ln\left(\sigma_g\right)^2\right)}$$

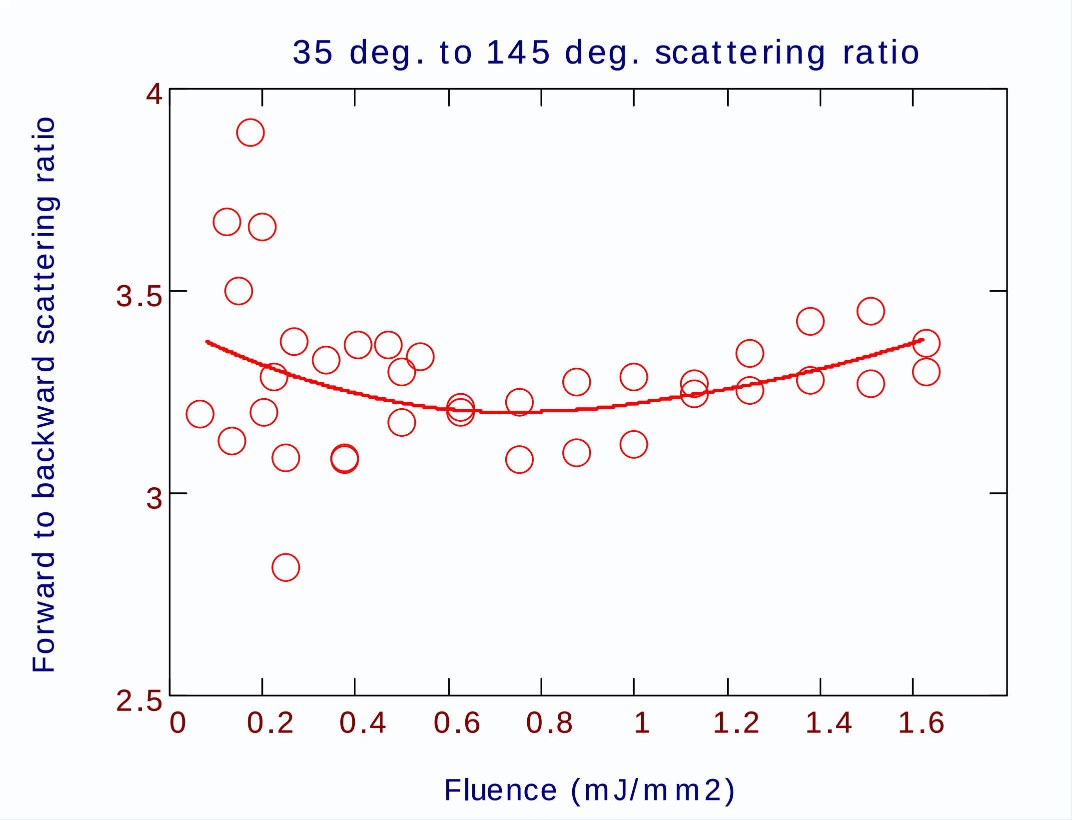
- the *F*(*m*)/*E*(*m*) ratio for soot in wide variety of flames has been summarized [3], with *F*(m_{532})/*E*(m_{532}) = 1.1
- *E*(*m*) is assumed constant from 400 to 780 nm

Forward and backward scattering coefficients



- the volumetric scattering coefficient is shown for forward scattering (35 deg, upper curve) and backward scattering (145 deg, lower curve) for three independent experiments

Forward-to-backward scattering ratio



- the forward-to-backward ratio gives an independent estimate of aggregate size and requires no knowledge of the scattering function

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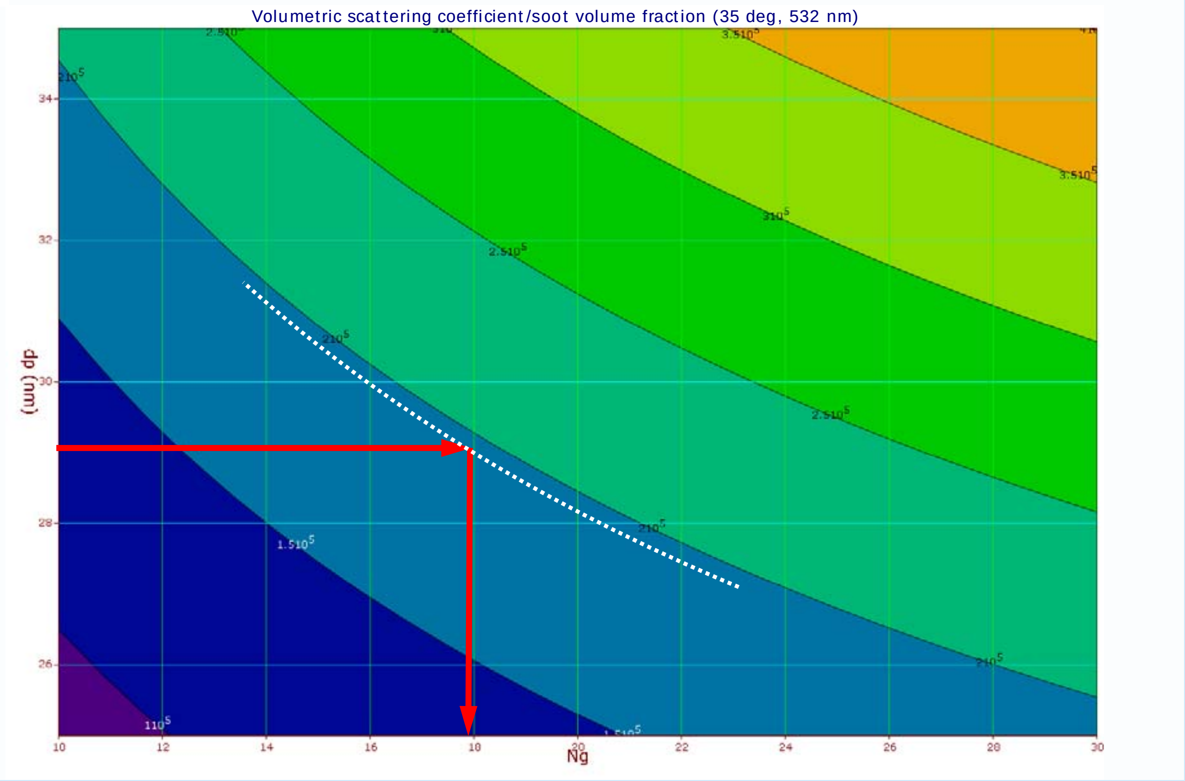
Numerical prediction – I



– given a primary particle size of 29 nm (from LII and TEM) and an average measured low fluence 35 degree volumetric scattering coefficient/soot volume fraction ratio of $1.91 \cdot 10^5$, the predicted N_g ~ 18

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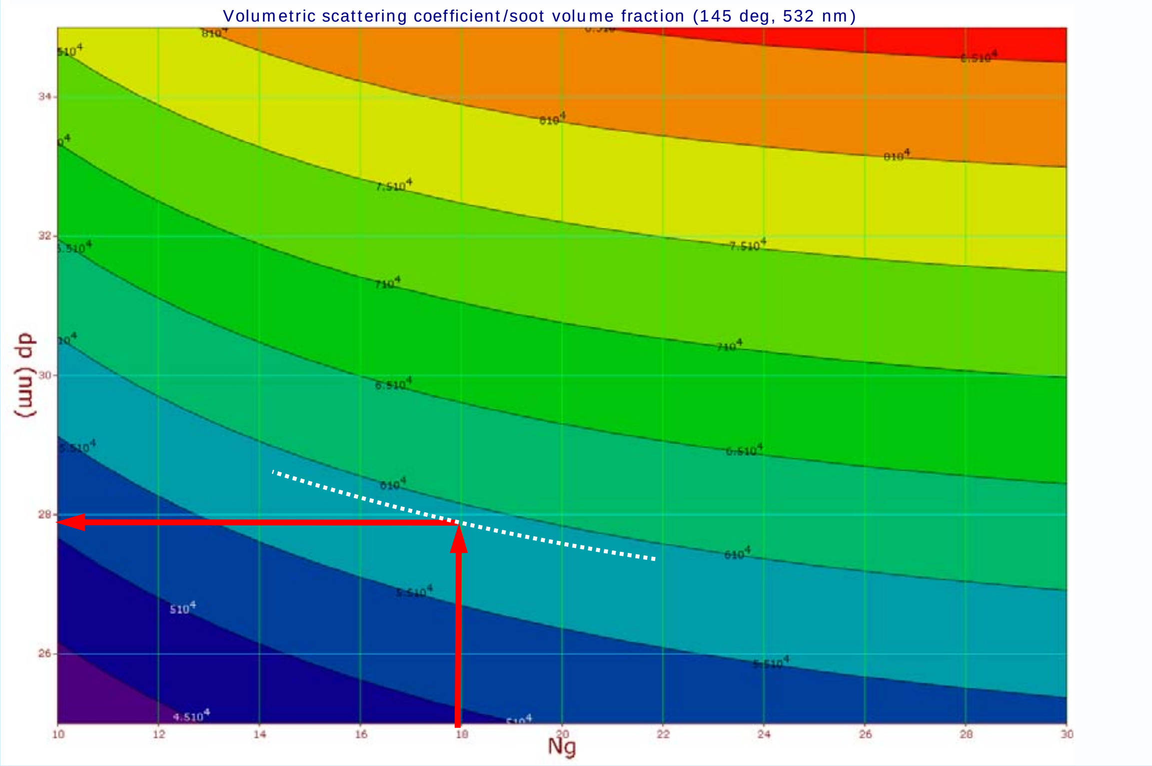
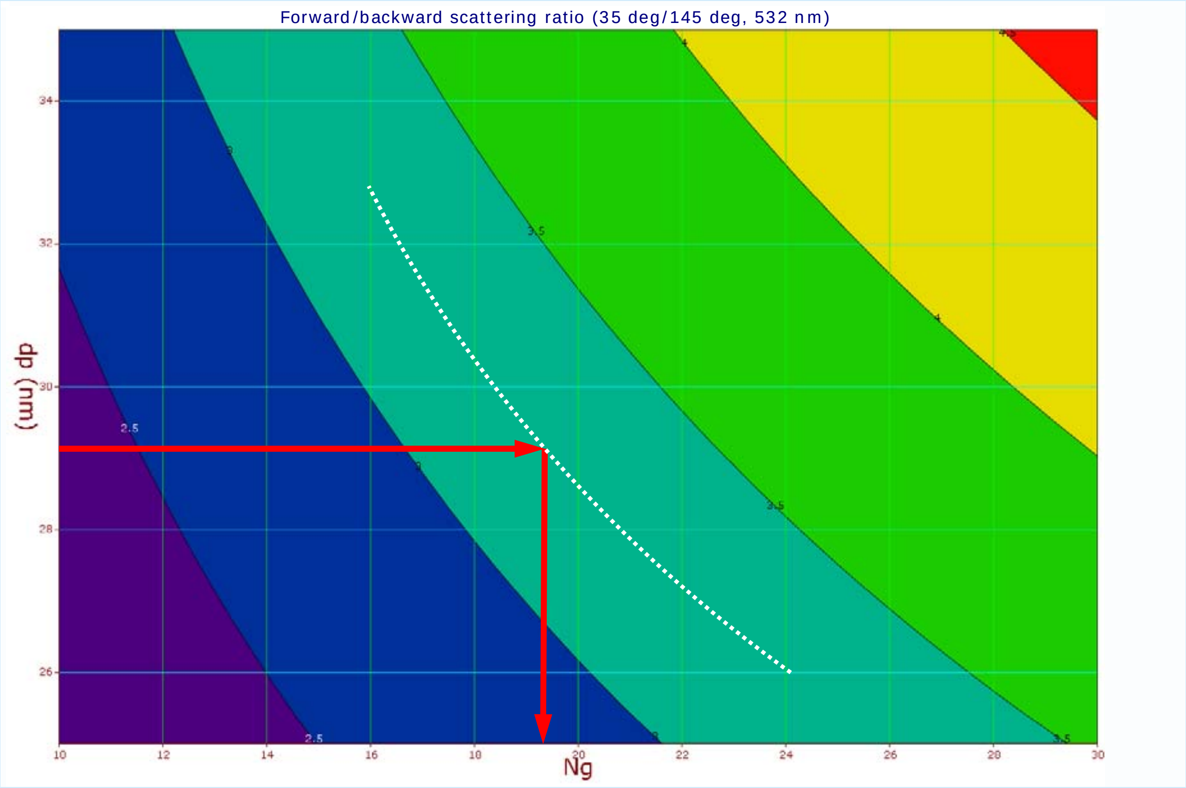
Numerical prediction – II



- the 145 deg volumetric scattering coefficient/soot volume fraction is insensitive to N_g but varies with d_p
  - the measured values of $5.81\cdot10^4$ and N_g=18 gives d_p ~ 28 nm, in good agreement with LII and TEM

Numerical prediction – III



- for a measured experimental forward/backward ratio of 3.25 and d_p=29 nm, N_g ~19

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Summary of results

- forward scattering and LII soot volume fraction give N_g ~18
- forward to backward scattering ratio gives N_g ~19
- TEM gives N_g ~21

- reasonable agreement

Conclusions

- an estimate of the mean aggregate size of an assumed lognormal distribution of aggregates can be derived based on the ratio of laser scattering to LII signal
- these values are in agreement with those obtained from forward to backward scattering ratio and TEM

Sub-Task 3.4S

Advances in Nanoparticle Characterization

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There have been major advances in the understanding of the physics and chemistry related to the nano-scale 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. The processes attracting the most attention are the heat and mass transfer processes that govern energy transfer in laser-induced incandescence. A recent workshop series on the science of LII has been established, with the first meeting held in Duisburg, Germany in September, 2005, and the second in Bad Herrenalb in August, 2006. This workshop series will continue on a two-year cycle, occuring just before each International Combustion Symposium, with the next workshop scheduled for July 31 – August 1, 2008, in Ottawa, Canada. Three key themes have evolved from the workshops, namely theory and modeling, experimental procedure, and signal evaluation for LII. The international LII community has established a web presence for the sharing of information about the science of LII, with results from the recent workshops, a forum, and a comprehensive bibliography of literature. The website is located at http://liiscience.org.

There are three contributions to report under this sub-task that address some of the theme areas identified above, plus the morphology of the soot nanoparticles through the development of a combined LII and laser light scattering technique:

Determining the Mean Aggregate Size of Soot Particles with the Combination of Light Scattering and Two-Colour Time-Resolved LII

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Laser-Induced Incandescence (LII) has become a well established technique for measuring soot concentration and primary particle size. What is missing for a complete morphological description of soot is the aggregate size i.e. the number of primary particles making up the soot aggregate. Soot aggregate size distributions are described by a lognormal function whose distribution width is largely independent of the soot source and the (geometric) mean aggregate size. Given this relative insensitivity of the distribution width it is possible to determine mean aggregate size from a combination of absolute LII signals and near forward laser light scattering.

A modification of a typical 2-color time-resolved LII system that allows us to simultaneously measure 2 color LII and scattering from the 532 nm LII excitation source is described. Thus a single measurement can result in estimates of soot volume fraction, the primary particle size and the geometric mean aggregate size. The application of this *in situ* technique to soot in a laminar diffusion flame is described. The mean aggregates sizes derived in this way depend on a knowledge of the ratio of the soot absorption and scattering functions. The results obtained are compared favourably to those derived from the ratio of forward to backward scattering. This latter technique requires no knowledge of the absorption or scattering function values.

Introduction

The details of the morphology of soot/black carbon aggregates are necessary to assess the health and environmental impacts of these nanoparticles. Laser-induced incandescence (LII) has become a well established technique for measuring soot concentration and primary particle diameter. The objective of this work is to extend the capabilities of LII to include the determination of the mean number of primary particles per aggregate.

Soot aggregate size (number of primary particles per aggregate) distributions are described by a lognormal function whose distribution width is largely independent of the soot source and the (geometric) mean aggregate size. Due to the relative insensitivity of the distribution width it is possible to determine mean aggregate size from a combination of absolute LII signals and near forward laser light scattering.

Approach

Modification of a typical 2-color time-resolved LII system [1] allows simultaneous time-resolved measurement of 2-color LII and single-angle absolute scattering intensity from a 532 nm LII excitation source. A single measurement can result in estimates of soot volume fraction, the primary particle diameter and the geometric mean aggregate size. The mean aggregate sizes derived with this method depend on a knowledge of the ratio of the soot absorption and scattering functions.

This *in situ* technique is applied to soot in a laminar diffusion flame. An enhanced technique that requires no knowledge of the absorption or scattering function values, based on the ratio of forward to backward scattering, is also evaluated.

Soot volume fraction from 2-colour LII

The soot volume fraction (f_V) derived from LII (or absorption) is inversely proportional to the value of *E*(*m*) assumed:

$$f_v = \frac{V_{EXP}}{\eta\, w_b G_{EXP} \dfrac{12\pi c^2 h}{\lambda_C{}^6} E\left(m_{\lambda_C}\right)\left[e^{\frac{hc}{k\lambda_C T_p}} - 1\right]^{-1}}$$

where η is the calibration factor, T_{pe} is the equivalent particle temperature, *G* is the amplifier gain, w_e is the equivalent laser width, *V* is the potential, λ_C is the centre wavelength, and *E*(*m*) is the absorption function. The property determined by LII is the product of soot volume fraction and the absorption function.

Soot scattering theory

Interpretation of the laser light scattering from the soot particles is based on Rayleigh-Debye-Gans Polydisperse Fractal Aggregate (RDG-PFA) theory [2]. The aggregate differential scattering cross section is:

$$\sigma_{ag} = N^2 \frac{\pi^4\, d_p{}^6\, F(m)}{4\,\lambda^4} S\left(q, R_g\right)$$

where *N* is the number of primary particles per aggregate, d_p is the primary particle diameter, and $S(q,R_g)$ is the structure factor. The scattering vector, $q(\theta)$, is defined as:

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

and the fractal radius of gyration, R_g, is:

$$R_g = \left(\frac{N}{k_f}\right)^{\frac{1}{D_f}} d_p$$

The structure factor is calculated numerically using the confluent hypergeometric approach [2], which assumes a Gaussian fractal cut-off. For a distribution of aggregates the scattering cross section must be integrated over the appropriate distribution function. The lognormal distribution:

$$P_{lognorm}\left(N, N_g, \sigma_g\right) = \frac{\exp\left[-\left[\left(\dfrac{\ln(N) - \ln\left(N_g\right)}{\sqrt{2}\,\ln\left(\sigma_g\right)}\right)^2\right]\right]}{N\,\ln\left(\sigma_g\right)\sqrt{2\pi}}$$

where N_g is the geometric mean aggregate size and σ_g is the distribution width is an appropriate distribution function for *N*.

To derive N_g from the ratio of soot scattering to LII intensity and the known soot scattering and absorption functions we must assume a distribution width σ_g.

Sorensen [2] has shown that a self preserving or scaling distribution gives a more accurate description of the higher moments that describe scattering than does a lognormal distribution. A self preserving distribution is theoretically predicted from solving the aggregate coagulation equations over a wide range of conditions, and an aggregating system develops a self preserving scaling distribution. Lognormal distribution moments with a width of σ_g~2.5 are in best agreement with the scaling distribution up to the third moment, providing a reasonable approximation for the true distribution width. Experimental evidence for flame soot shows σ_g~2.6. As this is in close agreement with the theoreticcal value of σ_g~2.5, the experimental value is assumed correct and is used for the subsequent analysis.

Volumetric scattering coefficient

The volumetric scattering coefficient is defined as:

$$C_{vol} = N_{ag}\sigma_{ag} = \int_1^\infty P_{lognorm}\left(N, N_g, \sigma_g\right) N^2 \frac{\pi^4\, d_p{}^6\, F\left(m_{532}\right)}{4\lambda^4} \times S\left(q, R_g\right) dN\, \frac{f_v\, 10^{-6}}{\dfrac{\pi\, d_p{}^3}{6} N_g \exp\left(0.5\ln\left(\sigma_g\right)^2\right)}$$

which is integrated over the lognormal distribution. The soot volume fraction from LII is inversely proportional to the value of *E*(*m*) assumed at the LII wavelengths. This allows substitution of the requirement to know the relative value of *E*(*m*) from 400 to 780 nm and the ratio *F*(*m*)/*E*(*m*) at 532 nm for a knowledge of the absolute values of the coefficients. The volumetric scattering coefficient then becomes:

$$C_{vol} = \int_1^\infty P_{lognorm}\left(N, N_g, \sigma_g\right) N^2 \frac{\pi^4\, d_p^{\,6}\, F\left(m_{532}\right)}{4\lambda^4\, E\left(m_{532}\right)}$$

$$\times S\left(q, R_g\right) dN \frac{f_v\, 10^{-6}\, E\left(m_{532}\right)}{\frac{\pi\, d_p^{\,3}}{6} N_g \exp\left(0.5 \ln\left(\sigma_g\right)^2\right)} .$$

The $F(m)/E(m)$ ratio for soot from a wide variety of flames has been summarized [3], with $F(m_{532})/E(m_{532}) = 1.1$ for a wide range of flame conditions. $E(m)$ is assumed constant from 400 to 780 nm, so that the absorption function at 532 nm can be used for both LII detection wavelengths.

Results

The volumetric scattering coefficient is shown in Fig. 1 for forward scattering (35 degrees from the forward direction, upper curve) and backward scattering (145 degrees from the forward direction, lower curve) for three independent experiments, each for a range of low, moderate, and high fluences.

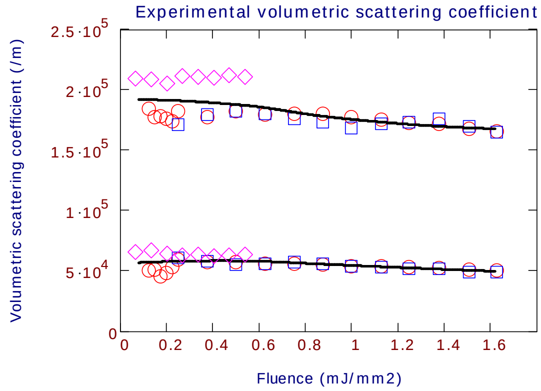

Figure 1

The forward-to-backward ratio, shown in Fig. 2, gives an independent estimate of aggregate size and requires no knowledge of the scattering function

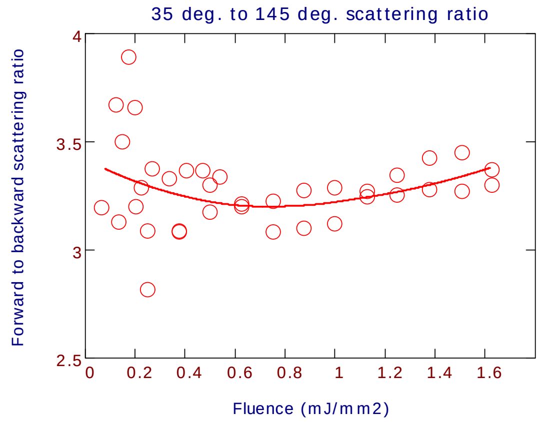

Figure 2

Given a primary particle size of 29 nm (from LII and TEM) and an average measured low fluence 35 degree off-axis volumetric scattering coefficient/soot volume fraction ratio of $1.91 \cdot 10^5$, the predicted geometric mean number of primary particles per aggregate is N_g~18, as shown in Fig. 3.

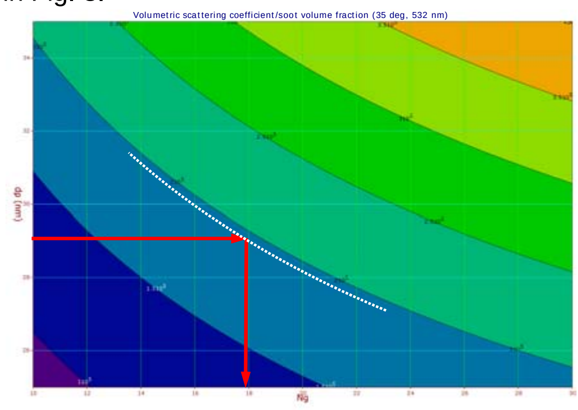

Figure 3

For the backward scattering case (145 degrees from the forward direction), the measured volumetric scattering coefficient/soot volume fraction ratio of $5.81 \cdot 10^4$ and N_g=18 from the forward scattering data in Fig. 3 result in d_p~28 nm, as shown in Fig. 4. This is in good agreement with the value of 29 nm determined by LII and TEM.

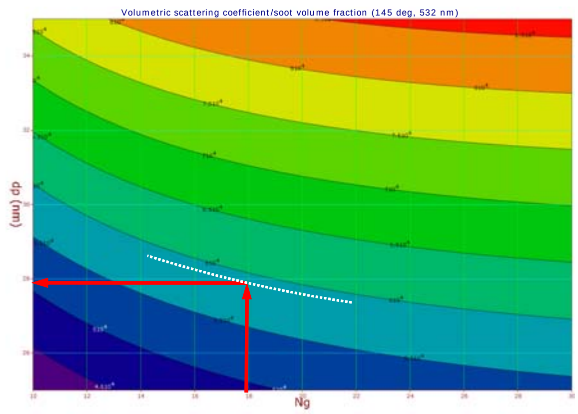

Figure 4

Note that the 145 deg volumetric scattering coefficient/soot volume fraction data shown in Fig. 4 are less sensitive to N_g than the 35 degree data shown in Fig. 3, but still show a significant dependence on d_p.

For a measured experimental forward/backward scattering ratio of 3.25 and given that d_p=29 nm (again from LII and TEM), N_g~19 nm, as shown in Fig. 5.

In summary, the results show that measuring forward scattering, combined with the soot volume fraction and primary particle diameter from LII give N_g~18. Measuring the forward-to-backward scattering ratio produces N_g ~19. Analysis of TEM images produced from thermophoretically sampled grids results in N_g ~21. The three techniques are in reasonable agreement with each other.

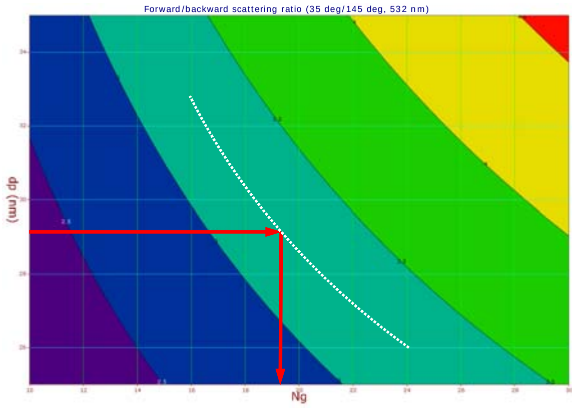

Figure 5

Conclusions

An estimate of the mean aggregate size of an assumed lognormal distribution of aggregates can be derived based on the ratio of laser scattering intensity to LII signal.

These values are in agreement with those obtained from the forward-to-backward scattering ratio and analysis of TEM images.

References

1. Snelling, D. R., Smallwood, G. J., Liu, F., Gülder, Ö. L., and Bachalo, W. D., "A calibration-independent laser-induced incandescence technique for soot measurement by detecting absolute light intensity," Applied Optics, 44, 6773-6785, 2005
2. Sorensen, C. M., "Light Scattering by Fractal Aggregates: A Review," Aerosol Science and Technology, 35, 648-687, 2001
3. Krishnan, S. S., Lin, K. C., and Faeth, G. M., "Extinction and scattering properties of soot emitted from buoyant turbulent diffusion flames," Journal of Heat Transfer, 123, 331-339, 2001

Assessment of Methods to Determine the Soot Absorption Function, E(m), and Implications for LII*

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A knowledge of the soot absorption function (E(m)) and its spectral variation is frequently necessary to interpret Laser-Induced Incandescence (LII) data. It is common to calculate E(m) from the soot refractive index, which, as is frequently noted, is quite uncertain resulting in large uncertainty in the resulting absorption function. Although knowledge of the refractive index is a sufficient condition for deriving E(m) it is not a necessary one. Far more reliable are the many direct experimental determinations of the absorption function that result from measured optical attenuation (corrected for scattering) with subsequent collection of the soot for gravimetric determination. Several groups have measured E(m) with this method and the variation amongst these measurements is typically ±30%.

More recently LII itself has been used to determine E(m) by a totally independent measurements that does not involve knowing the particle scattering or the soot density. We discuss the method and present new data for E(m) at 532 nm and compare this value with both our earlier determination of E(m) at 1064 nm and with the gravimetric calibrations over the visible wavelength and near IR wavelengths.

**Poster presented at the 2007 Gordon Research Conference on Laser Diagnostics in Combustion, Magdalen College, Oxford, UK, 12-17 August 2007*

Impact of Local Gas Heating During Time-Resolved LII*

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Laser-Induced Incandescence (LII) at high fluence can result in significant gas heating that must be taken into account when measuring LII signal decays. We present measurements of the gas heating resulting from laser excitation of soot for a laminar flame source containing 4 PPM soot. The data has been obtained for a range of laser fluences from low fluence where there is no impact to high fluence where there is gas heating and sublimation of the soot particles taking place simultaneously. The experimental results compare favourably to numerical estimates obtained from physical models based on the initial, CARS derived, temperature and the measured absorption coefficient at the 532 nm excitation wavelength.

The significance of this correction on cooling rate curves is described for a range of possible measurement scenarios. The variation in the cooling rates has a direct impact on the determination of primary particle diameter and active surface area from LII signals.

**Poster presented at the 2007 Gordon Research Conference on Laser Diagnostics in Combustion, Magdalen College, Oxford, UK, 12-17 August 2007*