Fourth International Workshop and Meeting on

Laser-Induced Incandescence: Quantitative Interpretation, Modeling, Application

April 18 – 20, 2010, Villa Monastero, Varenna, Lecco, Italy

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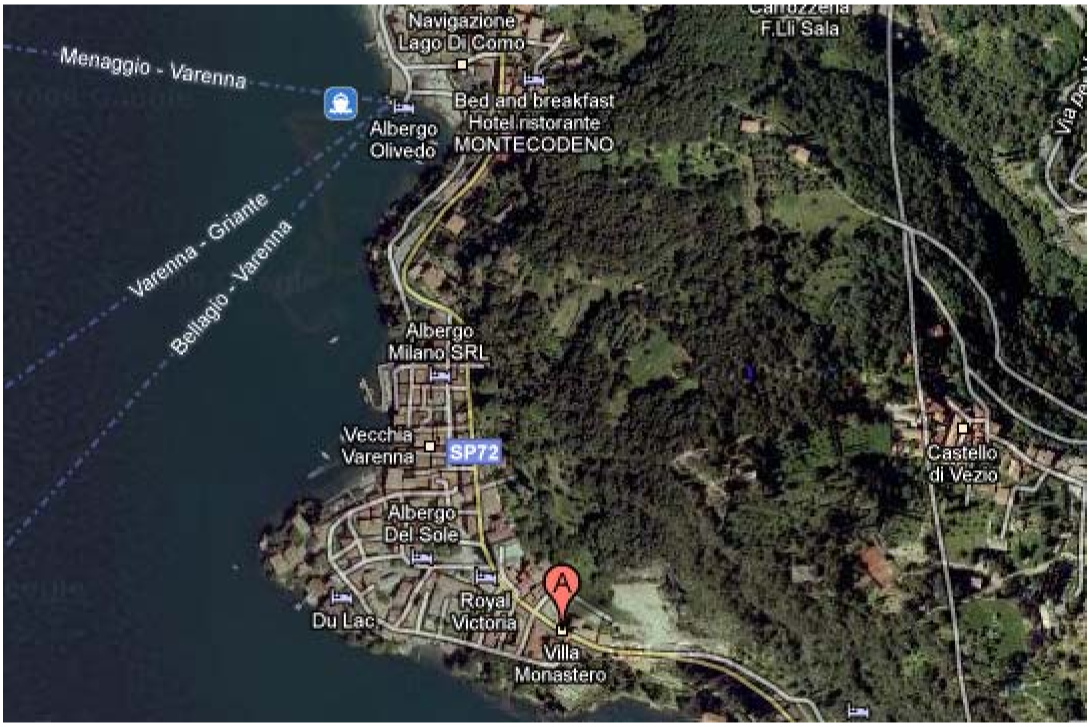
Fourth International Discussion Meeting and Workshop

Laser-Induced Incandescence: Quantitative Interpretation, Modeling, Application

SUNDAY, April 18, 2010

16:00	Registration and opening activities
18:00	Informal get together in Villa Monastero



MONDAY, April 19, 2010

08:30	Welcome and opening remarks
08:45	**Invited Lecture I01**. *H.H. Grotheer,* Laser-Induced Incandescence, Photo-ionization Mass Spectrometry (PIMS) and Soot Precursing Nanoparticles,

Session A – Soot properties and LII signal in standard flames

09:45	Papers presentation
09:50	**A01** - Determination of the refractive index wavelength dependence of Diesel and Diester soot by extinction spectra analysis, *J.Yon, E. Therssen, R. Lemaire, T. Amodéo, P. Desgroux, A. Coppalle, K.F. Ren*
10:10	**A02** - LII signal behaviour in a low pressure flame, *G. Cléon, P. Desgroux*
10:30	**A03** - Two-colour laser-induced incandescence for new insights into aggregation and optical properties in cold flows and flames, *J. Johnsson, N.-E. Olofsson, A. Bohlin, H. Bladh, P.-E. Bengtsson*
10:50	Coffee break and posters promotion
11:10	**A04** - Analysis of uncertainties in measurements of soot volume fraction using two-dimensional, auto-compensating, laser-induced incandescence (2D-AC-LII) applied to an ethylene diffusion flame, *B.M. Crosland, K.A. Thomson, M.R. Johnson*
11:30	**A05** - Influence of pulsed laser heating on the optical properties of soot, *P.Geigle, K.A. Thomson, G.J. Smallwood, D.R. Snelling*
11:50	**A06** - Wavelength and temperature dependences of the absorption and scattering cross sections of soot, *F. Goulay, P.E. Schraeder, H.A. Michelsen*
12:10	**A07** - Laser pulse accumulation effects on soot LII signals, *S. De Iuliis, F. Cignoli, S. Maffi, G. Zizak*
12:30	Organized discussion on Session A, *T. Dreier, S. De Iuliis*
13:00	Lunch

MONDAY, April 19, 2010

Session B – LII models and validation

14:30	Papers presentation
14:35	**B01** - Effect of particle aggregation on soot temperature determination in two-color LII experiments, *F. Liu, G.J. Smallwood*
14:55	**B02** - Modeling laser-induced incandescence of coated soot by a thin layer of Glycerol, *F. Liu, G.J. Smallwood*
15:15	**B03** - Comparison of LII model results with spectrally and temporally resolved measurements of LII from soot, *H.A. Michelsen, F. Goulay, P.E. Schrader*
15:35	Coffee break and posters promotion
15:55	Organized discussion on Session B, *F. Liu,H. Michelsen, H. Bladh*
17:00	Lake tour
20:00	Banquet dinner at Hotel Royal Victoria

TUESDAY, April 20, 2010

08:30	**Invited Lecture I02**. *A. D'Anna,* Properties of carbonaceous nanoparticles produced in combustion

Session C – Extending LII

09:30	Papers presentation
09:35	**C01** - Two-color TR-LII measurements of optical properties of growing particles, *A. Eremin, E. Gurentsov, K. Popova, K. Priemchenko*
09:55	**C02** - LII with continuous wave sources, *J.D. Black*
10:15	**C03** - Wide-Angle Light Scattering (WALS) for measurement of nanoparticle aggregates, *H. Oltmann, M. Altenhoff, J. Reimann, S. Will*
10:35	Coffee break and posters promotion
10:55	**C04** - Multi-Angle Light Scattering (MALS) for soot analysis: influence of aggregate polydispersivity on the structure factor, *O. Link, D.R. Snelling, K.A. Thomson, G.J. Smallwood*
11:15	**C05** - Soot morphology by combined LII and elastic light scattering, *D.R. Snelling, K.A. Thomson, O. Link, G.J. Smallwood*
11:35	**C06** - Soot characterization in premixed flames by TEM, extinction, multiangular scattering and LII, *S. Maffi, S. De Iuliis, F. Cignoli, G. Zizak*
11:55	**C07** - IR-laser ablation of species from growing soot particles and their detection through mass spectrometry, *K. Wolf, K. Thomson, F. Migliorini, H.H. Grotheer, M. Köhler, K.P. Geigle, G. Smallwood*
12:15	Organized discussion on Session C, *K.P. Geigle, S. Will*
13:00	Lunch

TUESDAY, April 20, 2010

Session D – LII under various conditions

14:30	Papers presentation
14:35	**D01** - In-cylinder measurements of the relative soot distribution in an optically access Diesel engine equipped with a production like bowl geometry, *R. Stirn, O. Heinold, G. Bittlinger*
14:55	**D02** - Investigation of soot formation in an optical access direct injection engine by means of LII, *D. Hertler, R. Stirn, S. Arndt, R. Grzeszik, A. Dreizler*
15:15	**D03** - Sooting turbulent jet flame: characterization and quantitative soot measurements, *M. Köhler, K.P. Geigle, W. Meier, B. Crosland, K.A. Thomson, G. Smallwood*
15:35	Coffee break and posters promotion
15:55	**D04** - Evaluation of particle size distributions by simultaneous application of TiRe-LII, PMS and TEM measurements to iron-oxide nanoparticles in a low-pressure flame, *B. Tribalet, H. Orthner, T. Dreier, C. Schulz*
16:15	**D05** - Laser-induced incandescence under vacuum at low pressures, *V. Beyer, C Hong Kam Him, D.A. Greenhalgh*
16:35	**D06** - Detailed analysis of particle dynamics in stationary and oscillating diffusion flames, *H. Bockhorn, M. Charwath, R. Suntz*
16:55	Organized discussion on Session D, *D. Greenhalgh, R. Suntz, K. Thomson*
17:30	Future plans and closing remarks
18:00	**End of the workshop**

Posters

P01 - Laser-induced incandescence during laser modification of Nickel nanoparticles from inert gas condensation, *M. Altenhoff, H. Oltmann, J. Reimann, S. Will*
P02 - Investigation of optical properties of aging soot, *F. Migliorini, K.A. Thomson, G.J. Smallwood*
P03 - Simultaneous single-shot imaging of temperature and soot concentration in ethylene nonpremixed flame containing soot, *Q.N. Chan, P.R. Medwell, P.A.M. Kait, Z.T. Alwahabi, B.B. Dally, G.J. Nathan*
P04 - Identification and analysis of PAH adsorbed on soot particles sampled from premixed low pressure methane flames, *A. Faccinetto, M. Wartel, M. Ziskind, C. Focsa, E. Therssen, P. Desgroux*
P05 - Validation of the values of the refractive index function ratios E(m, 266)/E(m, 532) and E(m, 532)/E(m, 1064) for the measurement of fluorescent species in liquid spray flames by coupling Laser-Induced Incandescence and fluorescence (LII/LIF), *R. Lemaire, E. Therssen, P. Desgroux, J. Yon, T. Amodéo, A. Coppalle and K.F. Ren*
P06 - Laser-induced incandescence of metal oxide nanoparticles generated in a laser vaporization reactor, *A. Flügel, J. Kiefer, A. Leipertz, H.-D. Kurland, J. Grabow, G. Staupendahl, F.A. Müller*
P07 - Using laser beam melting technology to design burner matrices for homogeneous sooting high-pressure flames for LII diagnostics, *M. Leschowski, J. Sehrt, T. Dreier, G. Witt, C. Schulz*
P08 - Soot concentration measurement in industrial plumes by retro-LII: principle, preliminary set-up and sensitivity investigation, *R.W. Devillers, K.A. Thomson, G.J. Smallwood*
P09 - Measurements in sooting laminar standard flames: LII and CARS, *K.P. Geigle, R. Hadef, J. Zerbs, M. Köhler, R. Sawchuk, D.R. Snelling*

Laser-Induced Incandescence, Photo-Ionization Mass Spectrometry (PIMS) and Soot Precursing Nanoparticles

H.H. Grotheer*
Institute of Combustion Technology, DLR
Pfaffenwaldring 38-40, 70569 Stuttgart, Germany

The paper attempts to highlight regions of interest common to both, the LII and the mass spectrometric community. Apart from particle size measurements, an important issue is the characterization of soot precursing nanoparticles which are readily accessible through PIMS and which might interfere LII experiments through their tendency to fragment. These precursing particles occur in bimodal form. Under LII irradiation an apparent third mode is generated as discovered in a joint LII-PIMS experiment. A closer view to these "particles" yields hints to the genesis of soot formation.

Introduction

LII and PIMS are linked through several overlapping areas of interest. An obvious one is that PIMS can measure particle sizes provided the density of the particles is known. PIMS thus furnishes a complementary measurement method in an adjacent size region. In fact, unlike LII, PIMS is not suitable for the measurement of mature soot since its "molecular weight" is in the range of 10^7 to 10^{11} u (atomic mass units) and this is far beyond the range accessible to PIMS.

PIMS is, however, particularly strong for the characterization of soot precursing nanoparticles. In comparison to soot these particles are quite unstable and hence may be expected to fragment under IR irradiation when fluences typical for LII are used. PIMS can not only provide information on nanoparticles, through its unique capability to measure gas phase species and particles simultaneously it can also be used to analyze LII fragmentation products (see [1]).

Whereas soot genesis is normally studied by pursuing the steps leading from gas phase precursors via nanoparticles and eventually to soot, analysis of soot fragmentation products provides a view on soot formation from the reverse side. It thus reveals new and interesting aspects concerning soot formation.

The contribution deals with four major topics:

- Advantages and limitations of PIMS for the measurement of particles.
- Characterization of soot precursing nanoparticles through PIMS, their differentiation upon interaction with UV light and their occurrence in and behind flames and behind engines.
- Summary of results obtained in a combined LII-PIMS experiment [1].
- Soot formation mechanism in the light of these findings.

A more detailed knowledge about soot precursors and very small particles can thus support understanding of the limiting factors for LII at its smaller size limit. In addition, PIMS can provide understanding the LII process, especially when approaching sublimation temperatures.

Experimental

An overview is given on several experiments ongoing or published recently [2,3] having the central elements in common. Species (molecules, precursors and particles) are sampled from various soot sources directly into high vacuum preventing further reaction or collisions. As an alternative to the frequently employed electron ionization we use high energy photons either at 248 (in some cases) or at 193 nm at sufficiently low fluence. This in combination with optimized time-of-flight ion detection allows us to measure gas phase species even beyond 3000 u at unity resolution and precursor species and particles up to 1 million u as distributions.

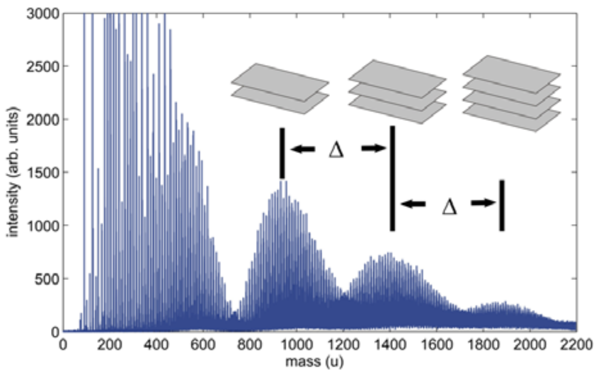


Fig. 1: Example of gas phase spectra mass resolution for one type of precursor species.

References

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[2] J. Happold, H.H. Grotheer, M. Aigner, Rapid Commun. Mass Spectrom. 21 (2007) 1247-1254

[3] T. Gonzalez Baquet, H.H. Grotheer, M. Aigner, Rapid Commun. Mass Spectrom. 21 (2007) 4060-4064

* Corresponding author: horst-henning.grotheer@dlr.de

Determination of the refractive index wavelength dependence of Diesel and Diester soot by extinction spectra analysis.

J. Yon[1*], E. Therssen[2], R. Lemaire[3,4], T. Amodéo[2], P. Desgroux[2], A. Coppalle[1] and K. F. Ren[1]
[1]CNRS UMR 6614 - CORIA, 76801 BP-12, Saint Etienne du Rouvray, France
[2] CNRS UMR 8522 - PC2A, 59655, Université Lille1, Villeneuve d'Ascq, France
[3] EMDouai, EI, 59500, Douai, France
[4] Université Lille Nord de France, 59000, Lille, France

The refractive index is an essential parameter in optical diagnostics of soot. It is necessary for quantitative interpretation of LII (Laser Induced Incandescence) signals, light scattering or extinction measurements and emissivity calculation. The most cited value of refractive index for soot particles was obtained using reflectometry method by Dalzel and Sarofim [1]. Nevertheless, this technique is ex-situ and needs a specific treatment of collected soot. Many values obtained by other methods are also available.

To our knowledge, only a few studies have been developed to take into account the complex morphology of soot particle and their size distribution. Krishnan et al. [2] combined gravimetric, extinction and scattered light for discrete wavelengths between 351.2 nm and 800.0 nm. Van-Hulle et al. [3] used extinction, scattered light and size distribution measured by a SMPS (Scanning Mobility Particle Sizer).

In the present study, a similar method to that used by Habib and Vervish [4] is applied for a shorter wavelength spectrum (350 nm to 1000 nm) but taking into account the soot morphology and size distribution whereas they used Mie theory.

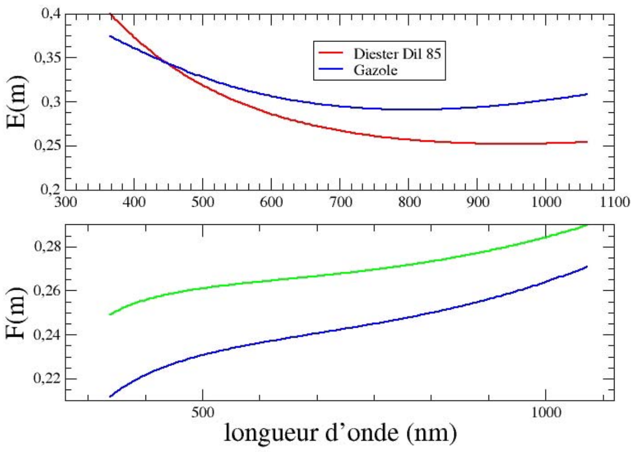

Fig. 1. Optical index of Diesel and Diester soot as a function of the wavelength.

Soot produced by Diesel and Diester spray-combustor [5] is sampled and injected into a tube of length 1.5 m. The extinction spectra through the tube is measured by a turbidity system [6]. At the same location, the soot size distribution $N(D_m)$ are measured by using a SMPS (3010-TSI). The particles morphology is also determined by analysis of Transmission Electron Microscopy images of particles sampled by thermophoretic technique.

That analysis enables the determination of soot morphological properties (fractal dimension d_f, fractal prefactor k_f and primary particle size D_p).

From the knowledge of size distributions and morphological parameters, the extinction spectra can be calculated according to the RDG-FA (Rayleigh-Debye-Gans theory for fractal aggregates) model. Indeed, the extinction coefficient is then given by:

$$K_{ext} = C_a\, E(m) \sum_{D_m} D_m^{d_f} N(D_m) + C_b\, F(m) \sum_{D_m} D_m^{2d_f} g(\lambda, D_m) N(D_m)$$

where the factors C_a and C_b depend on the morphological parameters d_f, k_f, D_p of the soot and the wavelength λ. The first and the second terms in the above equation represent respectively the contributions of the absorption and the scattering.

We can then determine the soot optical properties (E(m) and F(m)) by comparing the spectra calculated in this way and measured by turbidity. In order to perform this comparison without neglecting the scattering contribution to the extinction spectra, a dispersion model is used (Drude-Lorenz model). According to that simple model, E(m) and F(m) can be linked if some parameters are fixed. In our approach these parameters are determined by superposing the calculated and measured extinction spectra.

Using the dispersion model with the so determined parameters for Diesel and Diester combustion enable the calculation of the spectral dependence of the refractive index as presented in figure 1.

The obtained results will be compared with the ratio E(m,532)/E(m,1064) determined in situ by another approach (also presented at the LII workshop) based on LII signals [7].

References

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The authors thank the Agence Nationale pour la Recherche through contract ANR-06-BLAN-0349

* Corresponding author: jerome.yon@coria.fr

LII signal behaviour in a low pressure flame.

G. Cléon, P. Desgroux
CNRS UMR 8522 - PC2A, Bâtiment C11, 59655, Université Lille1, Villeneuve d'Ascq, France

In this work, the LII signal behaviour has been studied in a low pressure premixed $CH_4/O_2/N_2$ flame at 200 torr as function of the height above the burner, at different fluences and two excitation wavelengths: 532 and 1064 nm. It is shown that the behaviour depends on the reaction time i.e. on the maturity of the soot.

Experiment

We used a Mc Kenna burner (diameter is 60 mm) installed in a low-pressure vessel on a movable vertical support. The investigated flame is a CH_4:O_2:N_2 premixed laminar flame having equivalence ratio ϕ = 2.32 and P=200 torr. LII experiments were performed using a Nd:YAG laser operating at 1064 nm or 532 nm. The two laser beams are aligned with dichroic beam splitters and prisms so that their positions in the flame are perfectly coincident. A Top-hat configuration has been selected in both cases using relay imaging through a diaphragm of 2.5 mm diameter and using a lens of focal length= 500 mm. The position of the diaphragm and of the lens along the incident laser beam was adjusted at each wavelength to get exactly the same Top-hat profile (diameter = 2.3 mm) at the center of the burner. This was monitored using a CCD beam profiler (Gentec-EO Beamage). The broadband LII signal was collected at right angle using a set of two achromatic doublets (f_1 = 400 mm and f_2 = 200 mm) using a head-on photomultiplier (PMT Philips XP 2237). The 532 nm radiation was rejected using Notch filters. 500 laser shots were accumulated. The vertical spatial resolution along the flame axis was achieved by using a narrow (0.1 mm) horizontal slit parallel to the laser beam and placed in front of the PMT, which imaged the central part of the beam.

Results

Figure 1 shows the profiles of the soot volume faction and of OH radical measured by LII at 1064 nm and LIF respectively. Profiles of benzene, naphthalene, pyrene and temperature, have also been obtained in a parallel work by laser induced fluorescence–based methods in the same flame [1,2]. Fluence curves have been obtained at different locations in the flames. They are shown in figure 2 for a prompt detection after normalization at high fluence. An important variation is observed with HAB from the very young soot particles to mature soot particles far above the burner suggesting changes of physical properties of soot particles with reaction time. This confirms previous results obtained in the same flame by using a Gaussian laser [3].

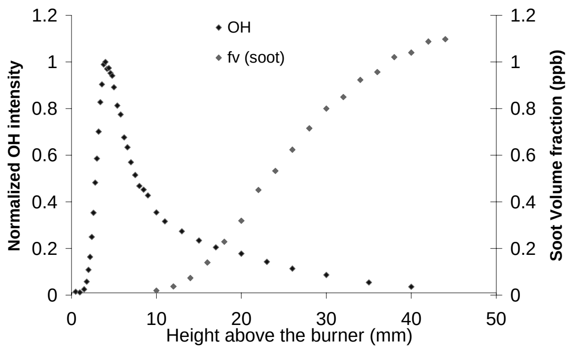

Figure 1: Soot volume fraction profile obtained by LII

The two-color method proposed in [4] has then been applied in view of determining the ratio of E(m) : E(m, 532nm)/E(m, 1064nm) along the flame. This method consists to select a couple of laser energies at 532 nm and 1064 nm insuring the equality of the LII signals in the low fluence regime under given conditions (facilitated here by the dual top-hat configuration). This equality means that the soot particle has reached the same temperature independently of the laser wavelength, i.e. the soot particle has absorbed the same energy. The absorbed energy being proportional to the laser irradiance times E(m), it can be shown that the ratio of E(m) can be easily determined by the ratio of the laser energies. Using this method we were able to observe an important decrease of E(m, 532)/E(m, 1064) along the flame.

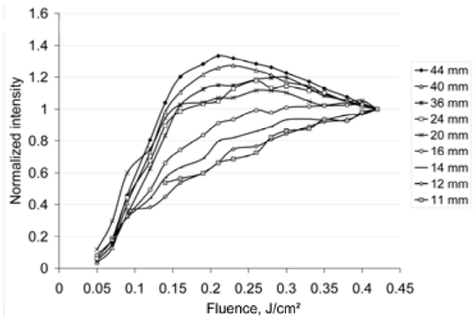

Figure 2: Fluence curves at 1064 nm

References
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[2] I. Burns et al., submitted
[3] P. Desgroux et al, Comb. Flame 155 (2008) 289
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The authors thank the Agence Nationale pour la Recherche through contract ANR-06-BLAN-0349

* Corresponding author: pascale.desgroux@univ-lille1.fr

Two-Colour Laser-Induced Incandescence for New Insights into Aggregation and Optical Properties in Cold Flows and Flames

J. Johnsson[1*], N.-E. Olofsson[1], A. Bohlin[1], H. Bladh[1], and P.-E. Bengtsson[1]
[1]Division of Combustion Physics
Lund University, Lund, Sweden

Properties of soot particles were measured in the soot growth region of a premixed flat ethylene/air flame and in the exhausts from a soot generator. Two-colour laser-induced incandescence (2C-LII) was used to calculate the primary particle sizes and $E(m)$ as function of height above burner in the flat flame. Aggregation effects on LII signals were tested experimentally in a cold soot stream from a soot generator.

Two-colour laser-induced incandescence (2C-LII) has been used to measure soot primary particle sizes in the soot growth region of a one-dimensional premixed ethylene/air flame on a bronze McKenna burner with equivalence ratio Φ = 2.1 and a co-flow of N_2. The maximum soot temperature from the two-colour pyrometry in 2C-LII was used together with rotational CARS gas temperatures and a theoretical model for LII to calculate $E(m)$ at 1064 nm. As shown in Fig. 1, it was found that evaluated $E(m)$ increases as function of height, if the soot density and specific heat capacity are assumed to be constant.

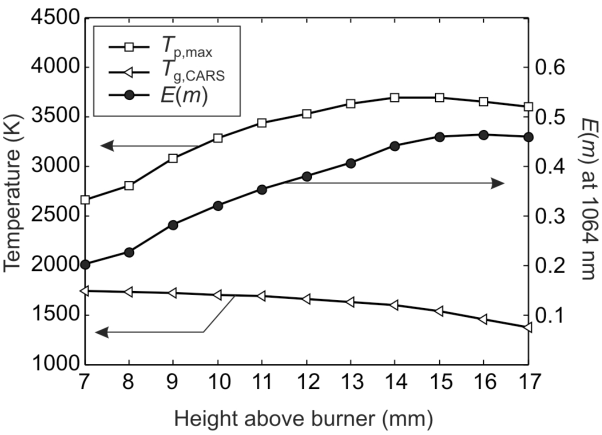

Figure 1: Evaluated data from measurements in the McKenna burner. The maximum soot temperature after laser-pulse heating, $T_{p,max}$, the gas temperature measured with CARS, $T_{g,CARS}$, and evaluated $E(m)$ are plotted as function of height above burner.

The primary particle sizes were evaluated using a theoretical model for LII, with a constant accommodation coefficient and without the aggregation term included. The 2C-LII sizes differed from those measured using transmission electron microscopy (TEM), especially at higher heights above burner where the soot starts to aggregate. The disagreement in the aggregated region may be explained by the fact that aggregation was not taken into account in the evaluation.

Aggregation effects on LII signals have been the focus of another investigation, where LII was applied in the exhausts from a soot generator, based on an ethylene/air diffusion flame quenched using a secondary gas stream. It has previously been shown theoretically that aggregation of primary particles results in a shielding effect with regards to the conductive heat transfer to the surrounding gas. An attempt to quantify the influence of aggregation on LII was made by comparing the time-resolved signals from LII measurements on soot produced using three different settings of the soot generator, cases A-C. The settings resulted in soot particles with similar primary particle size distributions but varying amounts of aggregation, as verified using TEM. The LII signals that were detected are plotted in Fig. 2, and show a clear dependence on aggregation level, with lower decay rates for higher levels of aggregation, in qualitative agreement with the theoretical results.

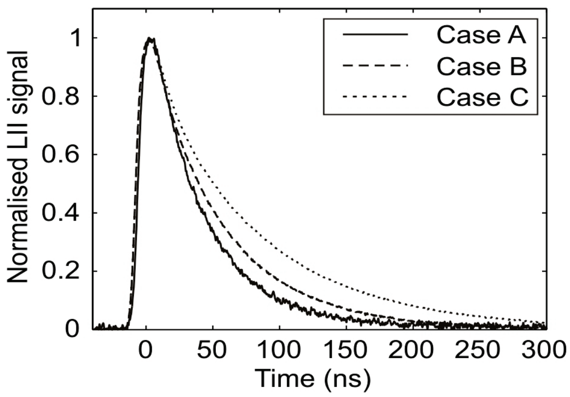

Figure 2: LII signals from soot from the quenched diffusion flame. The soot particles in cases A-C have different amounts of aggregation, but similar primary particle sizes.

* Corresponding author: jonathan.johnsson@forbrf.lth.se

Analysis of uncertainties in measurements of soot volume fraction using two-dimensional, auto-compensating, laser-induced incandescence (2D-AC-LII) applied to an ethylene diffusion flame

B.M. Crosland[1], K.A. Thomson[2*], M.R. Johnson[1]
[1]Department of Mechanical and Aerospace Engineering, Carleton University, Ottawa, Canada
[2]Institute for Chemical Process and Environmental Technology, National Research Council, Ottawa, Canada

We present soot volume fraction (SVF) measurements and a detailed uncertainty analysis of 2D-AC-LII with an eye toward using the technique for future instantaneous measurements. Agreement between both the instantaneous and average SVF measurements with attenuation measurements from the published literature is good. In the areas of strongest SVF the total uncertainty of an instantaneous SVF measurement is approximately +110%/-60% while the comparative uncertainty is approximately ±25%.

Introduction

Although development and application of AC-LII is progressing rapidly[1,2,3], 2D-AC-LII has received little attention to date[3] and has not been demonstrated with instantaneous measurements. We investigate the use of instantaneous 2D-AC-LII via a detailed analysis of the errors present in the measurement devices and physical quantities involved. The effect of these errors on the SVF calculation is determined via Monte-Carlo simulation.

Experiment

Experiments were made in a non-premixed laminar ethylene/air flame[4] at flow rates of 194 SCCM (20°C, 101.3kPa) and 284 SLPM, respectively. A pulsed Nd:YAG laser operating at 1064 nm was formed into a sheet with an average fluence of 1.3 mJ/mm^2. A beamsplitter directed the LII signal onto two ICCDs filtered at 442 ± 23 nm and 684 ±12 nm, respectively. The ICCDs were calibrated for spectral radiance and pixel response non-uniformity using a calibrated integrating sphere.

Measurements were taken with an ICCD gate width of 40 ns beginning 20 ns after the laser pulse peak. The CCD resolution is 22 µm per pixel, and 5x5 pixel binning was employed to increase signal-to-noise. The 1/e^2 laser sheet thickness is 130 µm.

Results

An instantaneous measurement is compared with published 2D line-of-sight attenuation (2D-LOSA) measurements[5] in Figure 1. The Monte-Carlo simulation yields a distribution of SVF for each measurement location. The 2.5 and 97.5 percentile of the distribution provide the limits of a 95% confidence interval for SVF.

Two Monte-Carlo simulations were performed to compare uncertainty from all sources of error to the uncertainty from only those that have an effect from one measurement to the next. In a location where SVF is 8 ppm, the total uncertainty is +9/-5 ppm and is dominated by uncertainty in the laser

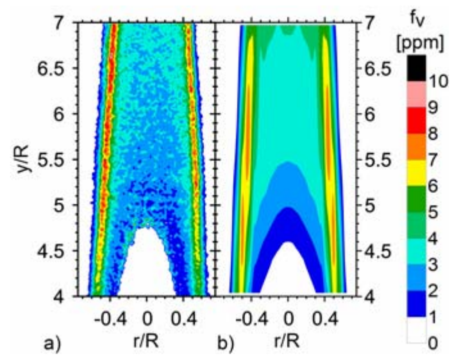

Fig. 1: a) 2D-AC-LII and b) 2D-LOSA measurements of soot volume fraction, f_v.

equivalent sheet width[6], the soot absorption function and the soot temperature. The comparative uncertainty is ±2 ppm and is dominated by photon shot noise and its effect on soot temperature uncertainty.

Conclusions

Instantaneous SVF via 2D-AC-LII shows good agreement with published results. The total uncertainty is quite high due to uncertainty in the optical properties of soot and its effect on both SVF directly and via determination of the laser sheet equivalent width. The comparative uncertainty is limited by photon shot noise, improvement of which will require an increase in the LII signal via changes to the experimental setup or via increased pixel binning during post-processing.

References

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* Corresponding author: Kevin.Thomson@NRC.ca

Influence of Pulsed Laser Heating on the Optical Properties of Soot

K.P. Geigle[1*], K.A. Thomson[2], G.J. Smallwood[2], D.R. Snelling[2]
[1] Institute of Combustion Technology, German Aerospace Centre (DLR), Stuttgart, Germany
[2] Institute for Chemical Process and Environmental Technology, National Research Council (NRC), Ottawa, Canada

Laser-induced incandescence (LII) is frequently described as an optical, non-intrusive diagnostic. However, it is well known that excitation at too high laser fluences is responsible for particle surface sublimation. This process is not well described by current LII models. In addition, several soot parameters introduced into LII modeling have to be approximated by those measured or extrapolated for graphite. The presented research focuses on monitoring changes of soot properties while LII excitation is applied.

Introduction

A cornerstone of the theory of laser induced incandescence applied to soot aerosols is that the soot is not affected by rapid laser heating. However, it has been demonstrated in the literature that intense laser irradiance typical of 'high' or 'plateau regime' LII leads to significant modification of the internal structure of soot particles [Vander Wal] and even the formation of new particles from vaporized material [Michelsen]. For moderate laser fluences typical of auto-compensating LII (AC-LII) [Snelling], morphological changes are not observable via high resolution transmission electron microscopy (HR-TEM) [Michelsen]; however, it is still conceivable that the rapid heating of soot aggregates to temperatures in the range of 3000 to 4000 K can influence the internal crystalline structure of soot as well as materials adsorbed on the surface and thus the optical properties of the soot may change as a consequence of the laser heating. Variation of the optical properties of the soot on time scales relevant to LII measurement would have impacts on the interpretation of signal which must be accounted for.

Experimental

In the present work, we monitor the extinction coefficient of a soot aerosol with time while simultaneously heating the aerosol with a laser pulse typical of LII. Measurements are made of the extinction coefficient at wavelengths of 405 and 830 nm and for a range of IR laser fluences. The cw attenuation laser monitors the central homogeneous portion of the pulsed IR laser beam when both concentrically travelling along a soot containing pipe. The incandescent emission from the soot is also monitored at wavelengths of 450, 557, and 750 nm close to the pipe exit to correlate the attenuation information to time-resolved soot temperatures.

Results

The variation of the extinction coefficient during and after laser heating is interpreted in terms of elastic and plastic variation of the soot refractive index absorption function, desorption and dissipation of adsorbed species, and sublimation. For low fluences signal changes are found to linearly correlate to changes of soot temperature. This behavior is expected when assuming a temperature dependent density or particle diameter (Fig. 1). In contrast, high LII laser fluences the particle density decrease, thus increase of attenuation is accompanied by diameter reduction due to surface sublimation. Implications of the performed experiments for LII measurement interpretation are discussed.

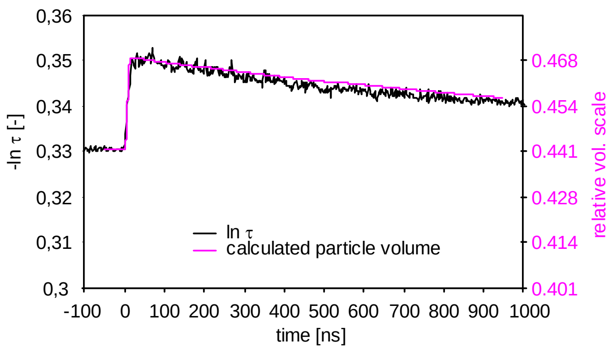

Fig. 1: Comparison of the attenuation at 830 nm measured during the LII process and relative volume based on LII modeling [4] for a reasonable particle size of 30 nm. The 1064 nm LII laser pulse at low fluence generates a change in attenuation starting from time zero.

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* Corresponding author: klauspeter.geigle@dlr.de
International Discussion Meeting and Workshop 2010: Laser-induced Incandescence, Quantitative interpretation, modelling, application

Wavelength and Temperature Dependences of the Absorption and Scattering Cross Sections of Soot

F. Goulay, P. E. Schrader, H. A. Michelsen*
Combustion Research Facility
Sandia National Laboratories, P.O. Box 969, MS 9055, Livermore CA, US

We have used laser-induced incandescence (LII) and transmittance measurements at 532 and 1064 nm to infer the wavelength and temperature dependence of the absorption and scattering cross sections of soot in a flame. The soot emissivity was found to deviate from the expected $1/\lambda$ dependence. The single-scattering albedos at both laser wavelengths confirm that scattering must be taken into account when interpreting extinction data at these wavelengths. Our results also indicate increases in the absorption cross section and decreases in the scattering cross section with increasing fluence at low fluences.

Introduction

Quantitative information about soot scattering and absorption cross sections is important for determining the impact of soot on climate and developing optical measurement techniques for soot particles. We have used LII to measure the relative absorption cross sections of soot at 532 and 1064 nm. Combining this result with transmittance through the flame, we inferred the value of the single-scattering albedo and the fluence dependence of the scattering and absorption cross sections of soot in the flame. We have investigated the effect of particle-size change with temperature on the scattering and absorption cross sections.

Experimental and results

Soot was generated in a nonsmoking laminar ethylene diffusion flame at atmospheric pressure using a Santoro burner. The particles were irradiated by a 532-nm or 1064-nm laser beam over a wide range of fluences. Soot emission was collected on a PMT with a 681.2-nm bandpass filter and with a fast gated-spectrograph. Transmittance was measured by sending the laser beam through the flame and detecting it before and after the flame using two pyroelectric detectors.

At low laser fluences the temporal peak of the LII signal is proportional to the absorption cross section, and the ratio of the 532- and 1064-nm fluences required to give the same peak LII signal is equal to the ratio of the absorption cross sections. Our results demonstrate that the wavelength dependence of the absorption cross section deviates from the $1/\lambda$ dependence derived using the Rayleigh approximation. Our results do not provide a functional form for the wavelength dependence of the emissivity but are consistent with the wavelength dependence reported by Köylü et al. [1,2].

Measurements of the transmittance provide information about the soot extinction cross sections. Using transmittance data and the ratio of the absorption cross sections, we inferred the single-scattering albedo and the fluence dependence of the absorption and scattering cross sections at both wavelengths. Our results yield values for the single-scattering albedo of 0.22-0.29 at 532 nm and 0.058-0.077 at 1064 nm.

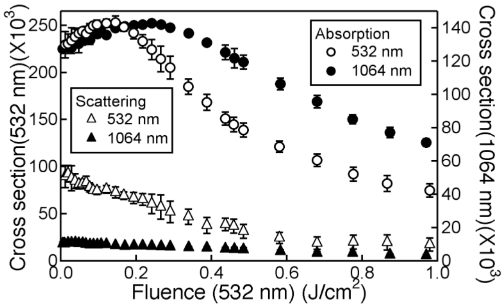

Fig. 1: Fluence dependence of the absorption and scattering cross sections for 532 and 1064 nm

Figure 1 displays the concentration-weighted absorption and scattering cross sections inferred from the combined LII and transmittance measurements. Sublimation leads to a reduction in particle size along with a reduction in scattering and absorption cross sections with increasing fluence above 0.14 J/cm^2 for 532 nm and 0.25 J/cm^2 for 1064 nm. At lower fluences, the absorption cross section increases with increasing fluence. Using soot temperatures derived from the spectrally resolved LII, we estimate a temperature-dependent particle-size increase that reproduces the measured absorption cross sections. The scattering cross section decreases with increasing temperature, which is inconsistent with the trend predicted if the primary-particle size increases with temperature. Alternatively the reduction in scattering cross section with increasing fluence could be due to a change in soot aggregate structure or a decrease in the reflectivity of graphite with increasing temperature.

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* Corresponding author: Hamiche@sandia.gov

Laser pulse accumulation effects on soot LII signals

S. De Iuliis, F. Cignoli, S. Maffi, G. Zizak*
CNR-IENI, sede di Milano,
via Cozzi, 53 – 20125 Milano - Italy

The effect of multiple laser pulses reaching soot particles before an actual LII measure is investigated in order to gain some insight on soot changes due to rapid laser heating. It is shown that even low laser fluences can induce some soot transformation.

Introduction

In Laser-Induced Incandescence (LII) soot particles heating plays a fundamental role. Peak temperatures range from 3000 K up to more than 4000 K depending on laser fluence [1]. These temperatures are reached in ns and this rapid rise can induce remarkable changes in soot characteristics. This has been directly observed through TEM analysis [2] but on the whole not very many experimental data can be found in literature. On the other hand understanding the physical and morphological modification of soot particles is crucial for modeling and for a thorough knowledge of the phenomenology involved. In order to gain insight in this field a study has been performed on the behavior of soot undergoing a variable number of pulses with varying laser fluences, by using a two-color LII technique.

Experimental Method

Experiments have been carried out on mature soot generated from a quenched diffusion ethylene flame. Soot is sucked by a dilution probe and piped in a test cell. This consists of a 20 cm (8 mm i.d) pyrex tube having proper access for gases and laser beam. The laser beam is steered coaxial with the tube, with the possibility of changing both the pulse energy and frequency. A diaphragm limits the Gaussian laser beam diameter in order to avoid scattering from the tube walls. A Gentec Beamage Focus I is used to control the beam intensity distribution. The LII signal is detected through an optical fiber coupled with a splitting optics and two photosensor modules with proper bandpass filters centered on 530 and 700 nm.

LII signals are recorded through a fast oscilloscope changing three parameters: laser fluence (130-350 mJ/cm^2 averaged on the Gaussian laser profile), laser frequency (2-30 Hz) and measuring positions along the tube (entrance, middle, exit). The flow rate is kept constant at a value of 1l/min. In this way it is possible to correlate the LII signals, peak and decay time, with the number of pulses hitting soot before reaching the measuring position.

Results

it is necessary to point out that not all soot particles are always excited by the laser pulses and that the laser beam is slightly expanding through the tube. Figure 1 shows the ratio of the prompt LII signals for two fluences and for different number of pulses exciting soot particles before reaching the measurement position. Assuming that the maximum temperature for a single pulse at high fluence is 4000 K [1] it is possible to draw a secondary scale of peak temperatures.

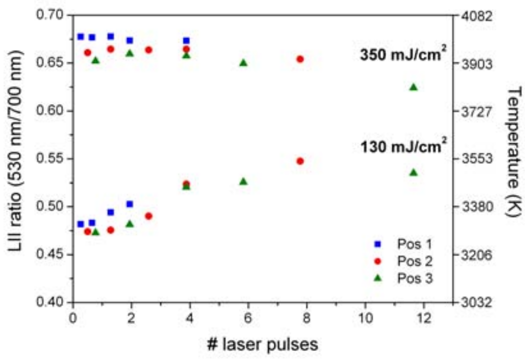

Fig. 1: Ratio of the peak LII signals at 530 and 700 nm for different laser fluences and number of laser pulses reaching soot before the measuring position

The figure shows that in the case of low fluence the peak temperature of soot particles initially increases with the number of pulses and then levels off. This can be interpreted as due to some physical transformation inducing an increase in the absorption coefficient. At high fluence the peak temperature is initially constant, indicating that soot transformation happens during the laser pulse. The temperature decrease, observed for an high number of pulses, is due to soot depletion, because of vaporization, in the central part of the laser beam leaving only soot particle at the edges of the beam to contribute mostly to the LII signal.

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* Corresponding author: zizak@ieni.cnr.it

Effect of Particle Aggregation on Soot Temperature Determination in Two-Color LII Experiments

F. Liu*, G. J. Smallwood
Institute for Chemical Process and Environmental Technology
National research Council, Ottawa, Ontario, Canada

Aggregation of soot particles results in mass fractal structure. It has been established that the particle aggregation makes the total absorption cross section of an aggregated soot particle deviate from the Rayleigh-Debye-Gans theory. This not only affects the ability of soot aggregates to absorb laser energy, but also their emissivity. This study investigates how aggregation affects the soot temperature derived from the signal ratio in two-color LII experiments.

Introduction

Increasingly research attention has been paid to the optical properties of fractal aggregates due to the fact that flame generated soot particles can be well characterized as mass fractal objects. Particle aggregations alter many physical and optical properties of soot compared to those of isolated, non-aggregated primary spherical particles. In the context of LII, it is important to quantitatively understand how aggregation affects the heat conduction behavior and the laser energy absorption rate of soot. Some efforts have been recently devoted to these aspects [1,2]. Since aggregation alters the absorption behavior of soot aggregates compared to that from the Rayleigh-Debye-Gans (RDG) theory, it is expected that their emission behavior is also changed accordingly. The emissivity of soot aggregates is required in the determination of soot temperature in two-color LII experiments, based on the ratio of LII signals detected at two wavelengths. However, the effect of aggregation on the soot temperature determination in two-color LII measurements has not been investigated. The objective of this study is to quantify the error of soot temperature caused by the neglect of aggregation effect.

Theory

For an arbitrarily shaped particle the emissivity is equal to its absorption efficiency [3]. Applying this principle to an aggregate leads to

$$Q_{abs}^{\ agg} = \varepsilon_p^{\ agg} \tag{1}$$

For an aggregate of size *N*, i.e., it consists of *N* primary spherical particles, its absorption efficiency is written as

$$Q_{abs} = C_{abs}^{\ agg} / (N A_{geo}^{\ p}) \tag{2}$$

where $C_{abs}^{\ agg}$ is the total absorption cross section of the aggregate and $A_{geo}^{\ p}$ is the geometric cross sectional area of a primary particle.

Two models were used to calculate the total absorption cross section of soot aggregates. One is the RDG theory for fractal aggregates and the other is the numerically exact generalized Mie-solution method (GMM). Aggregation effect is neglected in the RDG theory but is fully accounted for in the GMM results. GMM calculations were conducted for λ = 400 nm and 800 nm, d_p = 45 nm, and a constant refractive index of *m* = 1.6 + 0.6*i* to represent a typical value of soot in the visible. Representative results are shown in Fig. 1. For a given signal ratio (400nm to 800nm) the corresponding temperature can deviate from that based on the RDG model by about 100 K. Such an error in the soot temperature can lead to larger error in the soot volume fraction in the absolute LII intensity method [4]. The effect of soot particle aggregation on soot emissivity should be accounted for in the determination of soot temperature in two-color LII measurements.

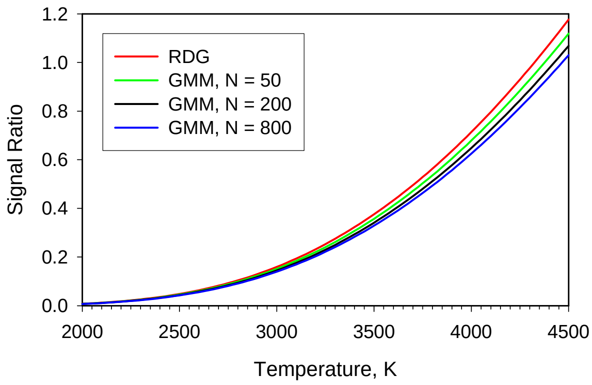

Fig. 1 Radiation intensity ratio from soot aggregates at 400 nm and 800 nm in the temperature range of 2000 to 4500 K for d_p = 45 nm and a constant refractive index m = 1.6 + 0.6i.

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* Corresponding author: Fengshan.liu@nrc-cnrc.gc.ca
International Discussion Meeting and Workshop 2010: Laser-induced Incandescence, Quantitative interpretation, modelling, application

Modeling Laser-Induced Incandescence of Coated Soot by a Thin Layer of Glycerol

F. Liu*, G. J. Smallwood
Institute for Chemical Process and Environmental Technology
National research Council, Ottawa, Ontario, Canada

To understand the potential impact of condensed organic compound on laser-induced incandescence measurements of soot from diesel engine exhaust, an LII model developed for dry, uncoated soot particles was extended for a coated soot particle by glycerol, which acts as a surrogate of condensed matter on soot emitted from engines. The shell/core model was employed in the formulation of the energy and mass conservation equations of a coated primary soot particle. The temperature of the coated soot particle was lower than the uncoated one due to some loss of absorbed laser energy to the evaporation of the liquid coating layer.

Introduction

Particular matter (PM) emitted from diesel engines consists of a significant amount of volatiles. Only the elemental carbon (EC) portion of the emitted PM responds to the pulsed laser heating to produce incandescence single in LII experiments. The presence of organic volatile compounds in the PM can potentially affect the laser heating of EC and the subsequent heat and mass transfer processes. Therefore, it is important to understand how the organic volatiles affect the temperature and particle size history during LII. Although the mixing state between EC and organic volatiles in PM can be quite complex, the simple shell/core model, where the EC forms a spherical core and the organic volatiles are treated as a shell enclosing the core, is still valuable to gain useful insights into the effect of organic volatiles on LII experiments conducted in diesel engine exhaust.

Almost all existing LII models were formulated for dry, uncoated soot particles. The only exception is perhaps the study of Moteki and Kondo [1], who formulated an LII model for a single spherical graphite particle based on the shell/core model.

Theory

Under the shell/core assumption, the energy and mass conservation equations can be formulated for a spherical coated soot particle having a diameter of d_p, which is the core diameter d_c plus twice the coating thickness δ. With the shell/core model, the laser energy absorption rate of the coated soot particle can be calculated using the Mie theory as given as the BHCOAT code [2]. The coating layer was assumed to be glycerol in this study to simulate the organic volatiles in diesel engine PM, with its physical and optical properties taken from Moteki and Kondo [2].

Numerical results obtained with a laser wavelength λ = 532 nm, T_g = 400 K, p = 1 atm, m_c = 1.56 + 0.57i (soot), m_s = 1.474 (coating), d_c = 30 nm, δ = 2 nm, and F = 1.25 mJ/mm^2 indicate that the temperature of the coated soot particle is lower than the uncoated one by about 150 K and the coating liquid is fully evaporated before the peak of the laser pulse. The temperatures with and without coating are compared in Fig. 1. At a higher laser fluence, the temperature difference is somewhat smaller due to the greater sublimation cooling of the uncoated soot particle.

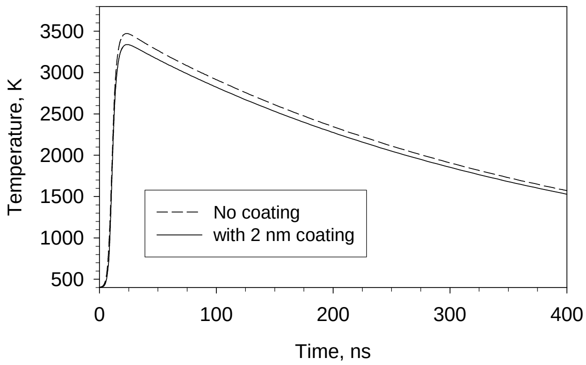

Fig. 1 Temperature history of the soot particle in the low-fluence regime with and without a 2 nm glycerol coating.

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* Corresponding author: Fengshan.liu@nrc-cnrc.gc.ca

Comparison of LII Model Results with Spectrally and Temporally Resolved Measurements of LII from Soot

H. A. Michelsen*, F. Goulay, P. E. Schrader
Combustion Research Facility
Sandia National Laboratories, Livermore, CA, USA

Current LII models do not reproduce spectrally and temporally resolved measurements of LII from flame-generated soot. Modeled temperatures tend to be too low at low fluences and too high at intermediate and high fluences. We have developed a model that demonstrates excellent agreement with measured temporal profiles of LII signal and temperature. Comparisons have been performed for laser wavelengths of 532 and 1064 nm over a range of fluence spanning two orders of magnitude. These comparisons are exploited to gain further insight into the physical and chemical mechanisms important in LII signal generation.

Introduction

Laser-induced incandescence (LII) involves heating the soot particles with a high-power pulsed laser to temperatures of approximately 2500-4000 K and measuring the radiative emission from the hot particles. This technique is used extensively to measure soot volume fractions and primary particle sizes under a wide range of conditions [1]. Model calculations are very useful for developing an understanding of the factors that influence LII signals. Such models must be validated against experimental data collected under well-controlled conditions. Recent experimental results provide temporal profiles of LII signals and particle temperatures recorded with laser wavelengths of 532 and 1064 nm and laser fluences between 0.02 to 3.5 J/cm^2.

Model comparisons with experimental results

Comparisons of current LII models to temporal profiles of temperatures and signals from laser-heated soot demonstrate significant problems with the description of LII generation and evolution. Experimental results demonstrate temperatures that increase more rapidly at low fluences than predicted using standard absorption coefficients. At higher fluences temperatures plateau at a value of 4000-4400 K, whereas models predict that the particles reach temperatures well above this range at such fluences [2]. Measured LII signals decay much more rapidly than predicted at these higher fluences.

To gain a better understanding of LII behavior, we have measured time-resolved LII signals from soot in an atmospheric laminar nonsmoking coflow ethylene diffusion flame over a wide range of laser fluences. A Nd:YAG laser was injection seeded to provide a smooth laser temporal profile with a pulse duration of 8 ns at 532 nm and 10 ns at 1064 nm, and the beam was passed through an aperture and relay-imaged into the flame to produce a smooth laser spatial profile. LII temporal profiles were recorded at 682 nm with a fast photomultiplier tube with adequate temporal resolution to capture signal evolution during the laser pulse.

We have also measured temporal profiles of particle temperatures during and following laser heating over a range of laser fluences. Particle temperatures were measured by spectrally and temporally resolving the radiative emission using a monochromator and a gated ICCD camera with a gate width of ~1.5 ns. Temperatures were derived by fitting the Planck function to measured spectra over the spectral range of 650-850 nm.

We used the temporal profiles of LII signal and temperature to aid in the development of a model that predicts the evolution of the physical characteristics of, and LII signal from, a laser-irradiated soot particle on a nanosecond time scale. By solving the energy- and mass-balance equations, this model accounts for particle heating by laser absorption and oxidation and cooling by sublimation, conduction, and radiation. The model also includes optional mechanisms for convective heat and mass transfer, melting, annealing, and nonthermal photodesorption of carbon clusters.

Conclusions

The new model agrees well with measured temporal profiles of LII signal and temperature throughout and well after the laser pulse as particles heat and cool. Good agreement between measured and modeled signals and temperatures is demonstrated over two orders of magnitude in fluence at irradiation wavelengths of 532 and 1064 nm.

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* Corresponding author: hamiche@sandia.gov

Properties of carbonaceous nanoparticles produced in combustion

A. D'Anna*
Department of Chemical Engineering
Università "Federico II" di Napoli, Italy

The paper focuses on the formation and properties of carbonaceous nanoparticles in flames and exhausts of practical combustion systems and on popular methods of sampling and detection of these particles. Particle chemistry is analyzed from data obtained by several measurement techniques. Nanoparticles show unique chemical composition and morphology; they maintain molecular characteristics in terms of chemical reactivity, but at the same time exhibit transport and surface related properties typical of particles. A modeling analysis is used to show how the growth of aromatics and the chemical nature of the particles depend on the combustion environment.

Introduction

Combustion of fossil fuels and biomass generates particulate matter ranging from micrometer-sized aggregates down to fine and ultrafine particles in the nanometer-sized range. For particles formed at high-temperature molecule to particle transitions are of nanometric size. They are difficult to intercept in the gas-cleaning devices and thus contribute to air pollution. The emission of these particles in the atmosphere contributes to photochemical smog and also constitutes a serious health concern. The in-situ, real-time measurement is a challenge for making combustion systems environmentally acceptable.

The mechanisms of formation and the physical and chemical characteristics of nanoparticles are not completely clear. We have the specific task of providing a detailed characterization of these particles for studies of atmospheric chemistry and toxicology.

Combustion generated nanoparticles have a unique chemical composition and morphology since they maintain molecular characteristics in terms of chemical reactivity, but at the same time exhibit transport and surface properties typical of particles. Many new diagnostic tools, which allow analysis on an almost atomic level have been developed, or borrowed from molecule-based natural sciences. Their use improves our knowledge about the physical and chemical properties of combustion-formed nanoparticles and also about the kinetics of particle formation in combustion environments.

Details about the formation of particles in combustion, particularly soot particles, have been reported in many research papers, comprehensive reviews [1-5] and published round-table discussions on soot held in the last 30 years [6-10]. The present work focuses on the processes by which nanoparticles with a diameter of 1–100 nm are produced from combustion systems. The paper mainly addresses formation and properties of nanoparticles in laminar, premixed and diffusion flames and in solid fuel combustion. Methods of sampling and detection of particles in the size range of interest are described. Also, particle chemical nature is analyzed, based on information gained from several measurement techniques. The formation of nanoparticles is reviewed in premixed and non-premixed laboratory flames and in the exhausts of practical combustion systems such as engines and commercial burners. The formation of nanoparticle during coal and biomass combustion is also analized. Finally a model of nanoparticle nucleation from the gas phase and particle growth in different combustion environments is discussed. The model is used to detail the internal structure of the particles and to show how the growth of aromatics and the chemical nature of the particles depend on temperature and on radical concentrations in the flames.

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* Corresponding author: andrea.danna@unina.it

Two-color TR-LII measurements of optical properties of growing particles

A. Eremin, E. Gurentsov*, K. Popova, K. Priemchenko
Department of Physical Gas Dynamics
Joint Institute for High Temperature, Moscow, Russia

The evidence of the change of particle refractive index function E(m) in dependence on particle size was found at TR-LII measurements of the soot growth induced by acetylene pyrolisis behind shock waves. The magnitudes of E(m) were found by the fitting of two independently measured values of particle heat up temperature, determined by two color pyrometry and from known laser energy. The small particles of about 1-8 nm in a diameter have a low E(m) - 0.05-0.1 which increases to the usual soot value of 0.3-0.4 during particle growth up to 20 nm.

Introduction

The reliable knowledge about refractive index function of nanoparticles is the great importance in LII and others optical diagnostics. A lot of investigations were devoted to the soot particles optical properties. The dependence of soot refractive index function on wavelength was discussed in a number of works (see for inst. [1]). The aim of this work is to get information about E(m) behavior with particle size.

Experimental

The soot particles were synthesized at pyrolisis of 3% acetylene in argon behind reflected shock wave in a diaphragm type shock tube. TR-LII measurements of soot particle sizes at different time delays up to 1.5 ms after reflected shock arrival have been carried out. The final particle sizes were analyzed by TEM. The Nd:Yag laser at wavelength of 1064 nm with Gaussian energy time profile and near top hat spatial profile is applied for particle heating. The laser fluence was varied in the range of 0.4-0.5 J/cm^{-2}. The LII signals were registered simultaneously at wavelength of 488 and 760 nm using narrow band pass filters.

LII model

The LII model is based on the energy and mass balance equations for current particle temperature during heating and cooling by surroundings and Plank's law for the LII signal calculation. The particle cooling takes place by conduction in free molecular condition, particle evaporation and thermal radiation. The fitting of value of particles heat up temperature measured by two color pyrometry and defined from known laser energy results in particle refractive index function E(m) [2]. The temperature dependence of soot heat capacity and log-normal distribution function of particle sizes were used for the calculations. On the base of the model the program code LII 1.0 was created for mean particle diameter extraction by least square fitting of calculated curve and experimental incandescence signal.

Results

The particles appear and grow during the reaction time after reflected shock arrival and acetylene pyrolisis start. The LII measured mean particle diameters are changed from 1-2 nm up to 20 nm. The values of E(m) extracted at wavelength 1064 nm are found less than this value for soot at the particle sizes under 20 nm. The dependence of E(m) on mean particle size is shown in Fig. 1 with the data for carbon nanoparticles at 266 nm [3] and for usual soot at 1064 nm [4].

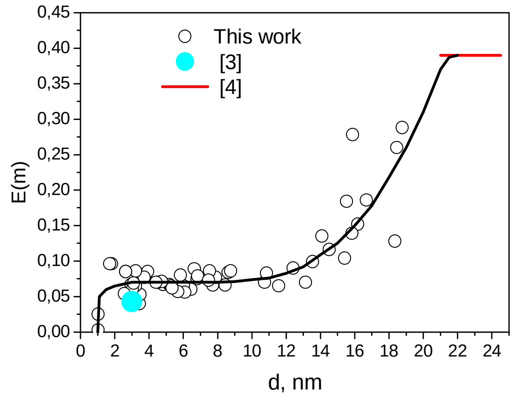

Fig. 1: E(m) versus mean particle diameter

At such low E(m) values the small particles couldn't get the evaporation temperature of graphite. On the other hand, the properties of such particles should be discussed separately.

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* Corresponding author: gurentsov@ihed.ras.ru

LII with Continuous Wave Sources

John D. Black,
School of Electrical and Electronic Engineering,
University of Manchester,
Manchester, M60 1QD, UK
John.black-2@manchester.ac.uk

Following the demonstration of LII in an engine exhaust using a long pulse fibre laser in 2007, experiments to characterize LII with CW laser sources are being carried out in sooting flames and in particles from a graphite aerosol generator. LII has been observed, by eye, in a flame using a focused near-infrared diode laser source at powers as low as 1.6 W. With the graphite aerosol, another process besides LII, with non-linear dependence on particle concentration, appears to be taking place when focused CW or millisecond pulse diode or fibre laser sources are used.

Introduction

Almost all LII work involves the use of nanosecond Nd/YAG lasers. However, this can be a severe disincentive to applying the technique in practical environments. Also, much more compact and efficient lasers, e.g. diode lasers and fibre lasers, in the power range required for LII are now available. These lasers can operate in CW mode or a very high rep rate with adjustable pulse length, but generally do not have the capability of producing nanosecond pulses. Experiments are in progress to characterize their effects in particle laden gas and to determine if they can be used for quantitative LII measurement.

Fibre Laser Experiments

An experiment was carried out using a manufacturing fibre laser (IPG Er fibre, power range 100 – 1000 W) and a Palas GfG1000 graphite aerosol generator. The laser was focused to a beam waist diameter of 60 µm and LII images from particles in an argon stream were recorded in both CW and pulsed (1 ms pulse, 50% duty cycle) modes. Particles were produced in an argon flow by discharge between carbon electrodes. The concentration was varied by diluting with more argon after the discharge.

With nanosecond pulsed LII, particles do not move appreciably during the laser heating pulse. However, with CW or long pulse lasers, the rate of movement of particles through the measurement volume must be taken into account. With increasing dilution, the velocity of the gas stream through the measurement volume increases. The Brownian velocity of a 30 nm diameter graphite particle at room temperature is ~15 ms^{-1}. Images were collected with a camera exposure time of 0.05 s and during this time many of the particles will have diffused out of the measurement volume, even if the gas was not flowing.

Sets of 100 images (each 0.05 s exposure) were recorded at various dilutions and averaged. The averages were divided by gas flow velocity and plotted against gas flow rate (proportional to concentration) to give Figure 1.

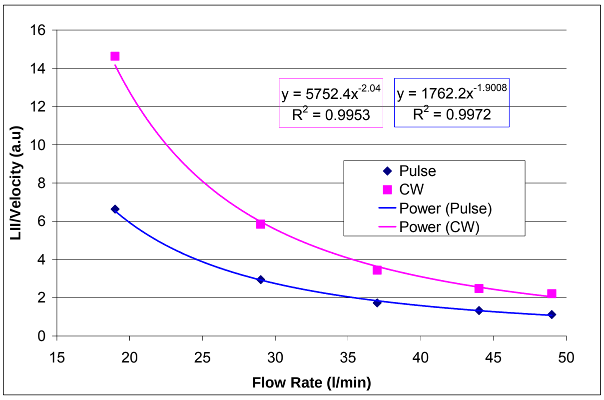

Figure1: Averaged LII signal divided by gas flow velocity plotted against gas flow rate

There is a remarkably good fit of the data to an inverse square relationship with flow rate in both CW and pulsed cases.

Diode Laser Experiments

A diode laser capable of producing 30 W CW at 803.5 nm (QPC Lasers Inc, BrightLase Ultra-50) has been used to generate LII in a flame and with the particle generator. The laser is fibre coupled and delivered through a 400 µm core diameter fibre. The fibre output is focused to a diameter ~ 500 µm in the measurement volume.

A bright zone where the laser traverses the flame can be observed by eye at powers as low as 1.6 W. Further analysis is in progress.

With the particle generator, localized very bright ‘flashes’ are observed intermittently at apparently random locations in the measurement volume. The frequency of flashes, and hence the total signal is dependent on laser power and particle concentration, but trends are not as clear as with the higher power fibre laser – investigations are continuing.

Wide-Angle Light Scattering (WALS) for Measurement of Nanoparticle Aggregates

H. Oltmann, M. Altenhoff, J. Reimann, S. Will*
Technische Thermodynamik, Universität Bremen, Germany

The application of wide-angle light scattering for the measurement of characteristic parameters of aggregates in combustion processes is demonstrated. The key feature of the approach is the use of an ellipsoidal mirror to collect scattered light over a wide angular range of about 10°-170° and to image it onto a CCD-camera. With this set-up an instantaneous acquisition of scatter diagrams with a high angular resolution of about 0.6° becomes possible. Results for the determination of radii of gyration are shown for soot particles in a flat flame burner under various conditions and for silica and tin dioxide particles produced in a diffusion flame and by flame-spray pyrolysis, respectively.

Introduction

Both soot and oxidic nanoparticles generated in flames usually exhibit a complex fractal structure. For a comprehensive characterization information on various geometric properties is required, including primary particle size, aggregate size and fractal dimension. While laser-induced incandescence (LII) basically offers the possibility to obtain primary particle size, this technique is - through shielding effects in heat transfer - influenced by aggregate properties. In order to provide this information elastic light scattering is employed with an approach that offers the possibility to simultaneously detect scattered light over a wide angular range.

Set-Up

Main components of the wide-angle light scattering (WALS) approach are a cw- or pulsed laser, an elliptical mirror and a CCD-camera. By the mirror and suitable lenses light scattered by particles in the probe volume is imaged onto the CCD-camera (Fig. 1). Through this approach light scattered within a plane is mapped onto the camera in form of a circle.

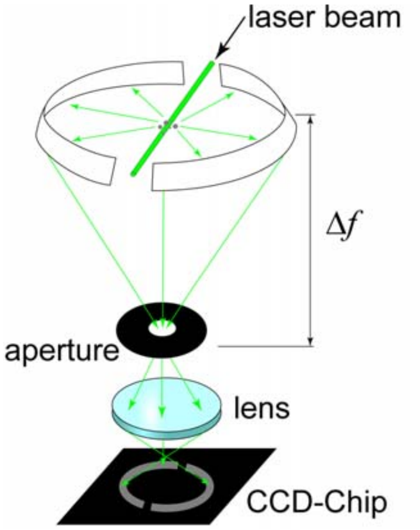

Fig. 1: Sketch of basic approach

With proper calibration of the optical properties of the set-up by scattering measurements on gases with known cross sections, scatter diagrams over an angular range between 10° and 170° may be obtained instantaneously with an angular resolution of 0.6° and below.

The performance of the approach is demonstrated by measurements on various types of particles using different types of burners. Measurements on soot particles were performed in premixed flames from a porous flat flame burner (McKenna type) operated with ethene and ethyne at various equivalence ratios. Additionally a diffusion flame operated with a gaseous precursor was employed to produce silica (SiO_2) particles, and a flame spray pyrolysis process was used for the synthesis of tin dioxide (SnO_2) particles.

Results

From the scattering diagrams the optical structure factor has been evaluated in the Guinier regime [1, 2] in order to determine aggregate radii of gyration R_g. In the measurements performed the R_g-values obtained span a wide range from 35 nm to 260 nm, and a good agreement with TEM data is observed. As with large aggregates the scattering data partly cover the power-law regime, the determination of the fractal dimension D_f becomes possible, too, and in the case of ethyne soot a fractal dimension $D_f = 1.7$ is obtained.

In summary, the WALS-techniques can be regarded as a powerful experimental tool for the characterization of gas-borne aggregates: it is applicable for a wide range of particle sizes and materials and favorably complements LII-measurements.

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Financial support by the German Research Foundation (DFG) is gratefully acknowledged.

* Corresponding author: swill@uni-bremen.de

Multi-angle light scattering (MALS) for soot analysis: Influence of aggregate polydispersity on the structure factor

O. Link*, D. R. Snelling, K. A. Thomson, G. J. Smallwood
Institute for Chemical Process and Environmental Technology
National Research Council Canada, 1200 Montreal Road, Building M9, Ottawa, K1A 0R6, Canada

A major shortcoming of LII is its inability to measure soot aggregate properties. Elastic light scattering, however, is a suitable method to provide these additional information [1]. The technique has been performed following different strategies, mainly in terms of the number of angles involved and the use of absolute or relative scattering intensities. The key quantity to express the relative angular scattering within Rayleigh-Debye-Gans (RDG) theory is the structure factor, which undergoes a subtle but significant modulation during the transition from a monodisperse to a polydisperse distribution, making it difficult to determine the size and polydispersity parameters simultaneously.

Introduction

This paper discusses the influence of a polydisperse aggregate distribution on the scattering structure factor. It points out how the derived radius of gyration is altered and how the analysis has to be adapted with respect to the monodisperse approach.

Theory and Results

Key to analyze the relative scattering curve is a proper understanding of how the intensity is modulated with angle. The behavior is expressed in terms of the structure factor, a quantity which is directly linked to the density autocorrelation function of the scatterer [2]. The structure factor of a polydisperse size distribution of fractal aggregates is obtained by employing the monodisperse expression and integrating over the size distribution

$$S_{poly}(\theta) = \frac{\int N^2 S_{mono}\left[\theta, R_g(N)\right] p(N)dN}{\int N^2 p(N)dN}. \qquad (1)$$

The general shape of the structure factor is preserved during the transition from a monodisperse to a polydisperse N-distribution. The Guinier and the power-law regime still exist and can be evaluated in an identical manner as in the monodisperse case, the Guinier regime providing the radius of gyration and the power-law regime providing the fractal dimension and the polydispersity parameter σ_g [2]. However, the radius of gyration derived from the Guinier regime is weighted by higher distribution moments. For a lognormal case these moments can be expressed in terms of the fractal dimension D_f and the distribution width σ_g

$$R_{g,gui} = \exp\left[(2D_f + 0.5)/D_f^2 \ln(\sigma_g)^2\right]\overline{R_g}. \qquad (2)$$

This shows clearly that referencing the two radii is only possible if D_f and σ_g are known. However, a characteristic of the structure factor modulation with increasing polydispersity is an extended cross-over regime between the Guinier and the power-law regime [3]. Thus, it gets cumbersome or even unfeasible to measure $R_{g,gui}$, D_f and σ_g simultaneously, also rendering the deduction of $\overline{R_g}$ impossible.

We suggest an absolute multi-angle scattering approach, which allows for a better determination of D_f and σ_g – which, however, depends critically on the uncertainty of additional input parameters (e.g. primary particle size, refractive index function F(m), fractal prefactor, and soot volume fraction).

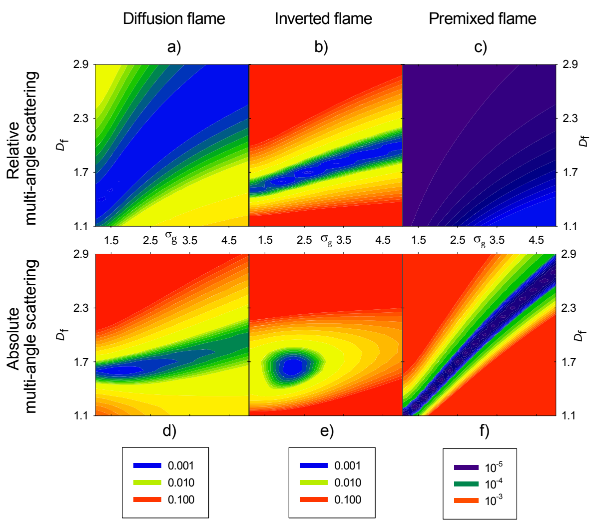

Fig. 1: Contour plots of residuals from RDG-fits to experimental MALS data in different soot samples (representing soot aggregates of different size).

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* Corresponding author: Oliver.Link@nrc.ca

Soot morphology by combined LII and elastic light scattering

D.R. Snelling, K. A. Thomson*, O. Link, G. J. Smallwood

Institute for Chemical Process and Environmental Technology,
National Research Council of Canada,
1200 Montreal Road, Ottawa, Ontario K1A 0R6

Soot emissions from flames are a common source of atmospheric particulates. To characterise physical properties of soot particles, the volume fraction (SVF), primary particle size (d_p) and soot aggregate size (the number of primary particles per aggregate, N) are useful parameters. While laser induced incandescence (LII) is now an established technique for measuring SVF and d_p, it is not able to provide sufficient information on aggregate size. We demonstrate the combination of elastic light scatter (ES) and LII for the simultaneous determination of SVF, d_p, and polydisperse distributions of soot aggregates using a self-preserving size distribution. It is shown how the combination of scattering angle and scattering wavelength in the scattering vector q, sets limits for the maximum detectable aggregate sizes.

Introduction

Elastic light scattering has long been used to measure mean soot aggregate size and the soot aggregate size distribution. The soot aggregate scattering depends on the higher moments of the distribution, which must be known to interpret scattering from polydisperse aggregates [1].

The combination of LII and light scattering offers a powerful tool in that it can potentially determine SVF, d_p and polydisperse aggregate size distribution parameters. In the present study we integrate LII and ES in a single instrument and use the ratio of the absolute light scattering to the absolute LII signal [2] to determine the mean aggregate size. In deriving the polydisperse aggregate mean size we make no assumptions as to the scattering regime, but solve the general RDG scattering equations. The results are compared to those obtained from Transmission Electron Microscopy (TEM) and two angle light scattering where the combined LII/ES was performed at two scattering angles

Experiment

The experimental apparatus, described in detail previously [2,3] was modified to include a photomultiplier in the detection module to monitor ES. The burner was a laminar co-annular ethylene/air flame [4]. Measurements are made on centerline at a height of 42 mm .

We measure SVF and the volumetric scattering cross sections at 35^o and 145^o from the forward direction. Assuming soot optical properties and the fractal parameters k_f and D_f we can derive an estimate of the aggregate size by two independent routes. The first method is to employ the ratio of two angle measurements of scattering. In the second method we dispense with the second scattering angle, instead ratioing the volumetric scattering coefficient to the SVF derived from LII.

Results and Discussion

Example volumetric differential scatter divided by SVF for the 35 and 145^o are shown in Figure 1. Consistent results are obtained for all fluences.

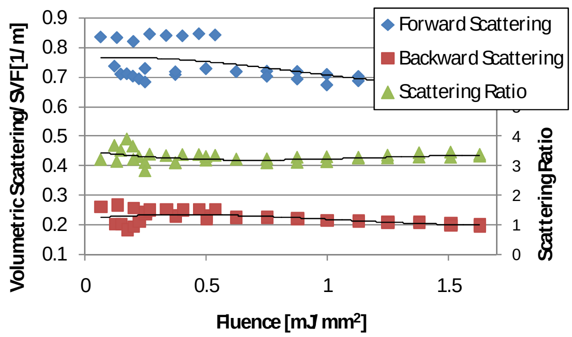

Figure 1 SVF normalized volumetric scattering and forward to backward scattering ratio

Both the 2 angle method and the forward angle combined with LII compare favourably with aggregate size determined from TEM images when self-preserving distributions are implemented. However, the theory indicates that the measurement of larger aggregates would require a smaller measurement angle than 35^o and that 90^o scattering would be incapable of sizing even the moderate sized aggregates found here.

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* Corresponding author: Kevin.Thomson@nrc-cnrc.gc.ca

Soot characterization in premixed flames by TEM, extinction, multi-angular scattering and LII

S. Maffi, S. De Iuliis*, F. Cignoli, G. Zizak
CNR-IENI, Istituto per l'Energetica e le Interfasi
Via Cozzi 53 – 20125 Milano, Italy

In this work different optical diagnostic tools are properly applied in order to gain information about soot characteristics in an ethylene/air premixed flame. By coupling extinction with three-angle scattering, measurements of soot volume fraction, radius of gyration and particle diameter are obtained. These results are compared with TEM and LII measurements.

Introduction

Laser-Induced Incandescence (LII) technique is a powerful tool for soot detection. One of the main topics about LII technique is the investigation of its dependence on the particle aging, that is on the presence of the so-called young and mature soot. In this work measurements are performed on an ethylene/air premixed flame (2.34 equivalence ratio), where different stages of soot formation can be detected along the flame axis, and by coupling different optical diagnostic techniques.

Experimental methodology

For extinction, a cw Nd:YAG laser beam (1064 nm) is focused on the flame axis and the transmitted intensity collected on the entrance of an integrating sphere. The signal is measured with a photo-sensor module (Hammamatsu H5783-01) and processed with a digital Lock-in amplifier (Stanford, model SR850 DSP), coupled with a mechanical chopper. Each signal results from an average over 300 samples.

For scattering measurements, the vertically polarized beam of a cw Ar^+Kr^+ laser (514 nm wavelength, Coherent Innova 70C spectrum) is focused on the burner axis with a lens (800 mm focal length). The scattered light is collected on a 1 mm slit facing a photomultiplier (Hamamatsu R4220) through an interference filter and a polarizer plate. The signal is processed with the digital Lock-in amplifier. Scattering signal is collected at 30°, 90°, and 150°. The burner is positioned on a goniometric platform with the receiving optics fixed on a mobile table, that can revolve on the goniometric plate.

As for TEM analysis, a thermophoretic sampling is applied to collect soot particles at fixed positions in the flame.

For incandescence measurements, a Nd:YAG laser beam working at 6 Hz (1064 nm) is used with a fluence kept constant at about 380 mJ/cm^2 [1]. A portion of the beam selected with a pinhole is imaged with a lens in the probe volume, in order to obtain a homogeneous top-hat cross section. The incandescence signal is collected by a mirror, focused on the slit of a monochromator and measured with a photomultiplier (Hamamatsu R955, 1.5 ns rise time) at 500 nm wavelength. The signal is detected and stored on a digital oscilloscope (Tektronix, 1 GHz, 5 Gs/s).The prompt LII signal is obtained by an averaging over a 4 ns time interval around the maximum.

Data analysis

The three angles scattering approach described in [2] is applied to the scattering angles 30°, 90°, 150°, based on fractal-like and RDG (Rayleigh-Debye, Gans) theories. Coupling these measurements with the IR extinction ones, the radius of gyration and the primary particle diameter are derived, which can be compared with the results obtained from TEM analysis (Table 1).

HAB	d_p (nm)		R_g (nm)	
	Optical	TEM	Optical	TEM
12 mm	17.90	16.47	19.63	19.23
14 mm	22.95	23.01	27.19	24.26

Table 1: Comparison of TEM and optical data.

TEM analysis allows also to derive the fractal prefactor, the fractal dimension and the distribution of both the primary particles diameter and the number of particles per aggregate.

Laser-Induced Incandescence intensities are properly scaled with soot volume fraction obtained from IR extinction measurements, giving the same structure of the axial profile. To complete the comparison of different techniques, so far quite satisfactory as resulting from Table 1, LII time decay analysis is currently in progress.

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* Corresponding author: deiuliis@ieni.cnr.it

IR-Laser Ablation of Species from Growing Soot Particles and their Detection through Mass Spectrometry

K. Wolf[2*], K. Thomson[1], F.Migliorini[1], H.-H. Grotheer[2], M. Köhler[2], K.P. Geigle[2], G. Smallwood[1]
[1]Institute for Chemical Process and Environmental Technology
National Research Council of Canada (NRC), Ottawa, Canada, K1A 0R6
[2]Institute of Combustion Technology, German Aerospace Center (DLR), 70569 Stuttgart, Germany

For the modeling and application of LII it is of interest to know whether there are species ablated from soot particles during IR irradiation, what kind of species are involved in these processes, and at which fluences the ablation occurs. This is highly demanded as current LII models for non-negligible sublimation conditions are not well predictive for the first tens of nanoseconds and strongly vary among different LII models [1]. A photoionization mass spectrometer, modified to allow IR and UV interrogation of a soot laden molecular beam and subsequent analysis of the ionized products, was employed to explore these questions. Autoionization C_n clusters were observed as a product of IR irradiation, while neutral ablation products were not detected via IR+UV conditions. A new size class of particles in the range of 1000 to 3000 amu appears promptly after IR excitation. These particles are most likely fragments of soot rather than agglomerates of C_n clusters.

Experimental Method

A premixed low pressure (100 mbar) C_2H_4-O_2 flame was used to generate particles under well controlled conditions. A quartz nozzle extracted a particle laden flow from the flame. Through a second nozzle a molecular beam was formed and fed via a skimmer into the mass spectrometer. The axes of the coincident laser beams, molecular beam and mass spectrometer, were mutually perpendicular to each other. Typically, an experiment was started by an IR pulse (4.2 ns duration, fluence between 0.1 and 10 mJ/mm^2, 1064 nm). After an adjustable delay of 0 to 10 µs the beam was probed by triggering the ion extraction of the MS with and without a UV pulse (8 ns, 193 nm, 1.6 MW/cm^2) timed with the ion extraction and normally used for photoionization mass spectrometry (PIMS). This UV fluence was determined to be insufficient for species fragmentation but suited for ionization. For a given set of flame and molecular beam conditions, a typical experiment consisted of a triple set, (i) UV alone to check the composition of the molecular beam with regards to gas phase and transition particles, (ii) UV + LII to check for any changes or enhancements induced by IR irradiation and (iii) IR alone to check for any creation of ions upon IR irradiation alone. Experiments of this kind were carried out as a function of IR fluence and of MS delay.

Results and Discussion

The fluence threshold upon which significant changes of ion spectra occur is around 1 mJ/mm^2, i.e. lower than previously reported and this may be attributed to the low pressure condition. A search for neutral gas phase volatilization products was essentially negative. There are only traces of C_2H_2 released from the irradiated soot particles and no PAHs for which our ionization is particularly sensitive.

What we obtained in the gas phase is the ladder of C_n clusters in the range 2<n<15 as shown in figure 1. Surprisingly, these peaks appear as ions, i.e they are detected without additional UV radiation.

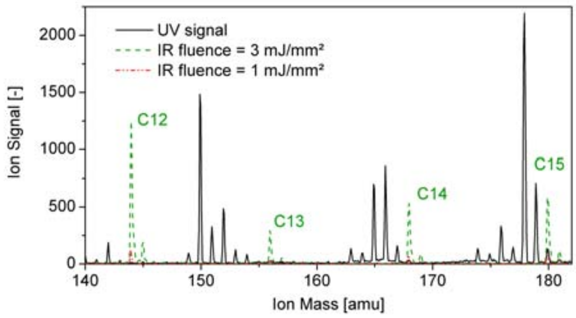

Figure 1: Mass spectrum of IR generated C_n cluster ions in comparison to UV spectrum

Another surprise upon IR irradiation was the instantaneous occurrence of a new apparent particle distribution in the mass range of about 1000 to 3000 u, which is also charged. This “peak” contains a C number of about two orders of magnitude above the C clusters. Therefore and because of its instantaneous formation it is not considered an agglomeration product of C-clusters. Rather it is thought to be ablated directly from soot. An analysis under higher resolution shows that it consists of a series of large PAHs. The studied phenomena should be supportive for improving the LII sublimation sub model.

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* Corresponding author: Katrin.Wolf@dlr.de

In-Cylinder Measurements of the Relative Soot Distribution in an Optical Access Diesel Engine Equipped with a Production like Bowl Geometry

R.Stirn*, O.Heinold, G.Bittlinger
Corporate Research – Engine Management and Mixture Preparation
Robert Bosch GmbH, Gerlingen, Germany

This contribution presents the result of our first 2D-LII measurements at our optical access Diesel engine. The main purpose of this engine is the optical investigation of new injection equipment and new injection strategies. In this first LII measurement campaign we focused on the variation of the Exhaust Gas Recirculation (EGR) to get an impression of the applicability and usefulness of this measurement technique for our questions.

Introduction

Due to more and more tightened emission laws it is essential to gain a deeper understanding of the underlying reaction and building processes of soot and other pollutants. With increasing knowledge of the ongoing processes it is possible to influence selectively the combustion by changing a great variety of parameters like, e.g. the nozzle geometry of the injection equipment, the injection pressure, the injection strategy or the exhaust gas recirculation (EGR). On the way to this understanding it is very important for the development of new injection equipment and engine management strategies to have powerful tools for the investigation of the consequences of changing one of the many parameters influencing the combustion. In addition to well established measurement techniques at Bosch, like Mie-Scattering and Schlieren for the review of the mixing preparation and high speed measurements of the soot luminescence there is an increasing necessity for the detailed investigation of combustion products at the region of formation. Besides the laser-induced fluorescence for combustion species we established the laser-induced incandescence (LII) for the in-cylinder measurement of - up to now - the relative soot concentration in our optical access Diesel and Gasoline engines.

Experiment and Results

The main focus during our first LII measurement campaign at this engine was the 3D - spatially resolved investigation of the influence of the exhaust gas recirculation rate on the formation of soot and it's correlation to the smoke number.

The engine operating point for this investigation was an emission test relevant part load condition with 1500 rpm at 4.3 bar indicated mean effective pressure (IMEP). The Diesel fuel was injected with a rail pressure of 700 bar and two pilot injections have been applied for the case without as well as for the case with EGR.

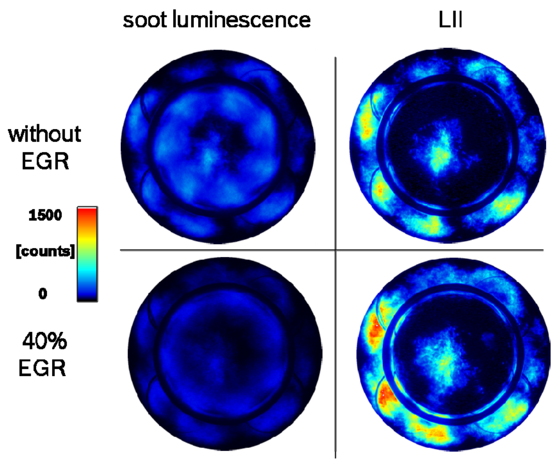

Fig. 1: Comparison of combustion with and without exhaust gas recirculation (vertical) and comparison of soot luminescence and LII signal (horizontal)

Fig.1 shows the results of a measurement 1mm above the piston crown at 20° ATDC. On the upper right hand side the LII-signal for the case without EGR is illustrated, below one can see the case with 40% EGR. On the left hand side the corresponding soot luminescence is shown which has been detected exactly 1µs before the LII signal with the same detection parameters. This comparison illustrates the danger of misinterpretation of the soot luminescence in an impressive way. Although there is significantly lower soot luminescence in the case with EGR there is in fact more soot at hand.

Conclusion

The significantly higher experimental effort - compared to high speed soot luminescence measurements - pays in cases where more detailed information is required. Especially the temperature independence and the 3D resolution are very attractive. Further measurement campaigns are planned in the near future.

* Corresponding author: ronnie.stirn@de.bosch.com

Investigation of Soot Formation in an Optical Access Direct Injection Engine by means of LII

D. Hertler*, R. Stirn, S. Arndt. R. Grzeszik, A. Dreizler*
Corporate Research – Engine Management and Mixture Preparation
Robert Bosch GmbH, Gerlingen, Germany / *CSI TU Darmstadt

This contribution contains the results of a comparison of time-resolved LII based on the model described by H.A. Michelsen [1] with further particle measurement systems, namely TR-SMPS and the determination of the Fuel Smoke Number (FSN). The intention was to cross-calibrate these different approaches. In this context several parameters like the air/fuel ratio or the injection pressure have been varied while using the measurement techniques in the exhaust of a gasoline direct injection engine.

Introduction

In recent years a change regarding the fuel injection of gasoline engines has emerged. An increasing number of automotive manufacturers offer direct injection gasoline engines in addition to the established engines with injection into the intake manifold and external mixture formation. In spite of several important advantages of the direct injection technique the soot formation of these engines became a serious challenge. Due to more and more restricted emission limit values concerning the gasoline engine it is essential to gain a deeper understanding of the underlying reaction and formation processes of soot and other pollutants. In addition to the limited values for the particle mass a limitation of the particle number will be introduced in Europe in 2014 and will be critical to satisfy without further measures. To optimize the combustion process by changing a great variety of parameters like, e.g. the injector type, the injection pressure and strategy or the ignition timing, it is essential to evaluate the particle formation and distribution with the help of qualified and reliable measurement techniques. In this context it is necessary to be able to perform in-cylinder measurement in an optical access engine beside the measurement in the exhaust gas system. Indeed there are only few measurement techniques known which provide detailed investigation of in-cylinder particle formation. Next to the soot luminescence which implies the danger of misinterpretation, due to the temperature influence, the Laser-Induced Incandescence (LII) is the most promising approach for in-cylinder measurement of soot formation in an optical access engine.

Realized Measurements

However, before using the LII-technique in the combustion chamber the main focus during the first measurement campaign was the application of the method in the exhaust system of a gasoline engine. In this context it was necessary to apply an optical access in the exhaust (Fig. 1). The basic idea of this approach is to cross-calibrate the results of the Laser-Induced Incandescence with further exhaust gas measurement systems [2]. Therefore a time-resolved Scanning Mobility Particle Sizer (TR-SMPS) and a Smokemeter have been established. With the help of the Smokemeter it is possible to determine the Fuel Smoke Number (FSN) while the TR-SMPS technique is able to specify the particle size distribution as well as the particle number.

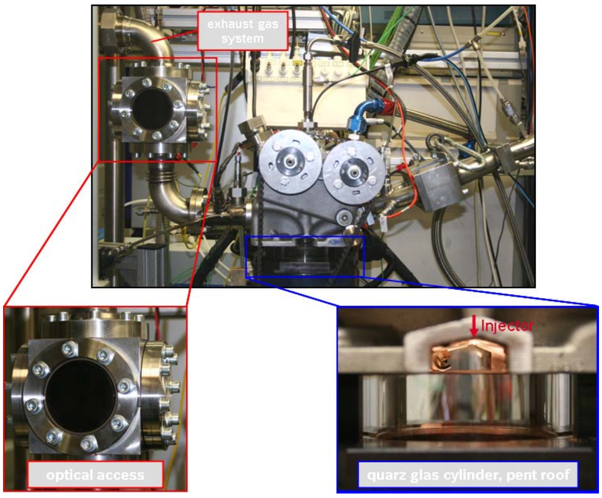

Fig. 1: Optical access engine with optical accesses to the exhaust system (left side) and to the combustion chamber (right side)

In a further step a comparison of in-cylinder measurements (LII) with exhaust gas measurements will be performed in order to get detailed information about the formation and oxidation processes of soot in a gasoline engine.

Conclusion

It can be summarized that a comparison of different particle measurement techniques has been successfully performed and a good agreement was found. These results are the basis for further measurement campaigns in the combustion chamber of a gasoline DI engine.

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* Corresponding author: daniel.hertler@de.bosch.com

Sooting Turbulent Jet Flame: Characterization and Quantitative Soot Measurements

M. Köhler[1*], K.P. Geigle[1], W. Meier[1], B. Crosland[2], K.A. Thomson[3], G. Smallwood[3]
[1]German Aerospace Center, Institute of Combustion Technology, Stuttgart, Germany
[2]Department of Mechanical & Aerospace Engineering, Carleton University, Ottawa, Canada
[3]Institute for Chemical Process and Environmental Technology, National Research Council, Ottawa, Canada

CFD modelers are strongly interested in high-quality data sets for validation of their numerical tools. Preferred features for a sooting test case are simplicity (no pilot flame), well known boundary conditions and sufficient soot production. Besides defining such a flame, setting up a comprehensive and accurate data base is challenging and requires optimization of sophisticated diagnostics including 2D-LII, CARS, PIV in order to characterize this complex transient sooting flame. The novel experimental database of soot properties, temperature and velocity maps can be used for the validation of kinetic soot models and numerical flame simulations.

Introduction

To improve soot predictions for gas turbine engines and industrial combustors, numerical simulation and kinetic soot model schemes need to be developed and validated that can accurately treat turbulent mixing, combustion and particularly the complex soot formation and oxidation chemistry.

Recently, comprehensive studies of turbulent non-premixed flames have been performed by several groups [1-3] to provide validation data. However, systematic measurements either have been conducted in complex piloted burners, large scale flames or provide very low soot concentrations.

The purpose of this work is to optimize existing data sets from sooting jet flames based on CFD needs a) by definition of a simple turbulent sooting flame and b) the acquisition of high-quality data sets from measurements of this new sooting "standard flame". Additionally, diagnostic challenges, limits, improvements and optimizations are discussed.

Experimental

Our goal is to provide a simple burner geometry without the need for a pilot flame, making numerical simulations less complex. In addition, the flame is short enough to have sufficiently well defined air flow boundary conditions even high up in the flame and reducing the number of measurement locations. Experiments were conducted in an atmospheric pressure ethylene jet flame (inner tube diameter of 2 mm). A co-annular air flow (inner diameter of 140 mm) serves as oxidizer. In order to guarantee well-established boundary conditions for flame modelling, the burner was mounted inside an optical housing to prevent disturbances from room-air. Desirable flame conditions were obtained with a fuel flow rate of 10.4 g/min and an air co-flow of 320 g/min, resulting in a lifted turbulent flame (Re=10000) with considerable soot concentrations. The visible flame height is approximately 40-50 cm, while the lift-off height shall provide a very sensitive criterion for CFD modelling.

2D-LII was obtained using the fundamental output of a pulsed Nd:YAG (1064 nm, 40 mJ sheet energy). The 2D-LII images were calibrated with line-of-sight extinction measurements at 1064 nm, suggested as a suitable wavelength for pure soot absorption[4]. Additionally, simultaneous symmetry tests were performed based on OH*.

To determine temperature statistics even in the rich burning and sooting regions of the flame on a single shot basis, we employed shifted-vibrational CARS. The system consists of a Nd:YAG laser pumping one narrowband (λ=591 nm) and one broadband (λ=685 nm) dye laser for multiplex N_2-CARS. Furthermore, simultaneous PIV and 2D-LII measurements have been realized with a Nd:YAG laser (532 nm) in order to characterize the flow field and investigate correlations with soot formation processes on a shot to shot basis.

Results

The 2D-LII experiments show that the new defined "standard flame" contains soot structures, detectable on a shot-to-shot basis with average soot concentrations of around 0.6 ppm.

The strong fluctuations affect the SV-CARS temperature measurements as well, showing location-dependent high dynamics in intensity. However, in combination with the measured velocity field (data analysis ongoing) and a still to be performed TiRe LII study, a comprehensive data set for model validation shall be available.

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* Corresponding author: m.koehler@dlr.de

Evaluation of particle size distributions by simultaneous application of TiRe-LII, PMS and TEM measurements to iron-oxide nanoparticles in a low-pressure flame

B. Tribalet*, H. Orthner, T. Dreier, C. Schulz
IVG and CeNIDE
University of Duisburg-Essen, Germany

The objective of the present work was to apply laser-induced incandescence with time-resolved detection (TiRe-LII) for particle size evaluation of iron(III) oxide (Fe_2O_3) nanoparticles synthesized in a low-pressure flame reactor. For comparison particle sizes were measured by simultaneous experiments with a particle mass spectrometer (PMS) and rapid particle sampling for transmission electron microscopy (TEM).

Introduction

LII has become a common method for in-situ analysis of particle size and visualization of particle volume fractions predominantly for soot diagnostics in a wide range of applications. Besides lower signal strength due to less strongly absorbing material and lower heat-up temperatures, one of the main challenges when applying LII to non-soot nano-particles is the poor data base of relevant particle thermophysical properties, e.g., heat conduction, accommodation coefficients, vaporization enthalpy and high-temperature chemistry for describing particle cooling due to convection, vaporization and other effects. The measured laser-induced radiation signals from synthesized iron oxide particles were evaluated in terms of particle sizing by using a modified version of the TiRe-LII model developed by Kock et al. [1].

Experimental

Iron oxide nanoparticles were synthesized in a premixed rich $Fe(CO)_5/H_2/O_2/Ar$ flat flame in a low-pressure flame reactor described in [2]. Fig. 1 schematically shows the main components of the experimental setup.

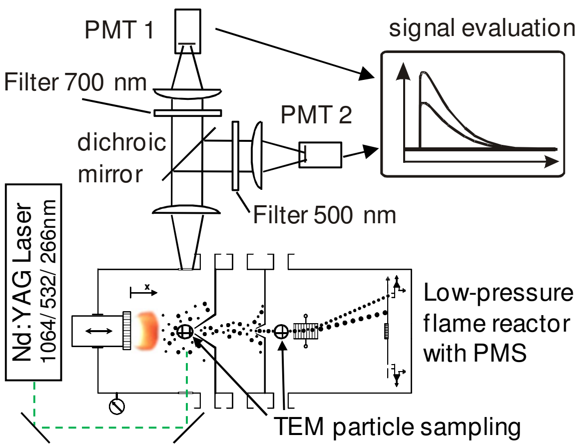

Fig. 1: Experimental setup

The pressure in the combustion chamber was kept constant at 35 mbar. By moving the burner relative to the fixed measurement location (i.e., laser crossing or nozzle sampling point, respectively) the residence time in the reactor can be varied. The required optical access to the measurement location was realized by three fused silica windows. For particle heat-up we used a frequency doubled, pulsed Nd:YAG laser (532 nm, E_{max} = 50 mJ/pulse) with a beam diameter of 4 mm. LII signals were recorded perpendicular to the beam axis by a two-color TiRe-LII detection unit, equipped with narrow band-pass filters with center-wavelengths at 500 nm and 700 nm respectively (FHWM = 20 nm) in front of two high-speed photomultipliers with integrated amplifiers.

As show in Fig. 1, for particle sampling TEM grids were alternatively moved into the LII measurement volume for thermophoretic sampling (without laser firing) and into the molecular beam after the sampling nozzles. The second location allows the sampling of particles after laser heating by the laser pulse for investigating effects on particle morphology and composition.

Results and discussion

The combination of independent measurement techniques allowed to evaluate the measured TiRe-LII signals in terms of particle sizing. Additionally, the influence of laser-induced particle heating on the particles was investigated by TEM. The combination of TiRe-LII and online molecular beam particle sampling with subsequent particle mass spectrometry in low-pressure flames is a promising approach for fundamental research on the characteristics of LII of various nanoparticle materials.

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* Corresponding author: benjamin.tribalet@uni-due.de

Laser-Induced Incandescence under vacuum at low pressures

Vivien Beyer[1*], Christopher Hong Kam Him[2], Douglas A. Greenhalgh[1]
[1]School of Engineering and Physical Sciences
Heriot-Watt University, UK
[2]Department of Mechanical Engineering
Imperial College, UK.

Laser-Induced Incandescence at low pressures is characterized by long signal decays (well over 50 microseconds are achievable) due to the predominance of radiative over conductive cooling. Moreover, low pressure LII has the potential to provide not only an insight into the very fundamental physics of LII such as sublimation, conductive or radiative cooling rates, but it also aspires to single nanoscopic entities measurements rather than ensemble-averaged quantities. We will present our most recent advances on the subject.

Introduction

Laser-Induced Incandescence under vacuum is defined by a nanoparticle surrounding gas pressure of less than 10^{-2} mbar, whereby heat conduction from the nanoparticle to the surrounding gas molecules cease contributing to LII signal decays [1]. The main interests of performing LII at low pressures are the capability to isolate physical phenomena such as sublimation, heat conduction, radiation and eventually annealing whereas higher pressures are systematically biased towards particle – gas collision heat losses. In addition, increased sensitivity and longer signals allow for finer measurements.

Experimental setup

Following our previous LII under high vacuum study of large soot agglomerates [2], we implemented an aerodynamic lens [3] system capable of bringing atmospheric soot nanoparticles into a focused 500 microns diameter particulate beam at pressures as low as 10^{-3} mbar with >90% transmission efficiency. LII is then provoked by a continuous and uniform 70x800 µm^2 laser beam profile delivered by a 1070nm 400W CW fibre laser as described in figure1. Fluences as low as 4.10^4 W/cm^{-2} proved sufficient to detect consistent LII signals with particles transit times through the laser beam of less than 1.5µs.The measurement region is characterized by a visible plume formed by incandescent particulate matter. Two-colour time-resolved LII signals are captured with two high sensitivity photomultiplier tubes at the centre wavelengths of 457nm and 784 nm with respective filter widths of 105 and 171 nm. Spectral measurements and TEM readings are also taken as reference.

Results and Discussion

Laser-Induced Incandescence measurements of temperature decays for characterized particulate matter will be presented for low pressure LII. A discussion of the measured respective heat loss rates for well-characterized nanoparticles will be provided. In addition, the experiment provides us with an insight into the relationship between aerodynamic diameter, soot morphology and measured single particles incandescent surfaces. Single nanoscopic entity measurements will be demonstrated together with our current limitations and future research directions.

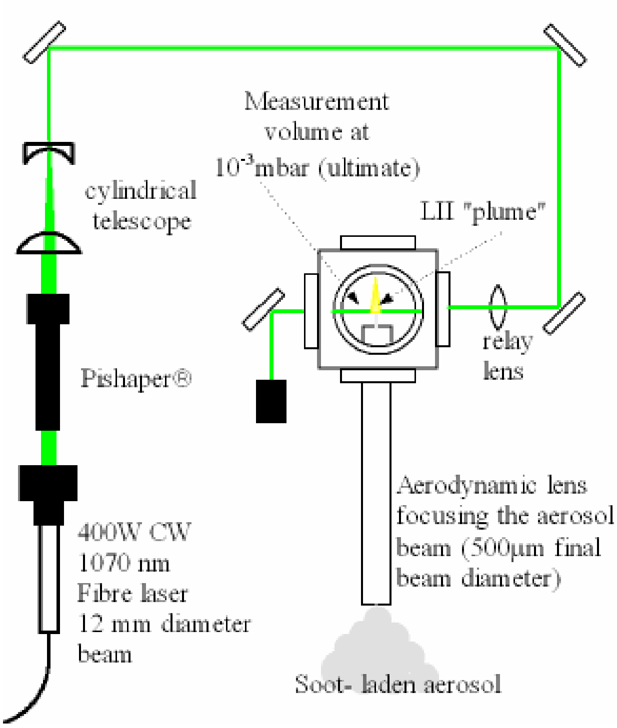

Fig. 1: Experimental setup

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*Corresponding author: v.beyer@hw.ac.uk

Detailed Analysis of Particle Dynamics in Stationary and Oscillating Diffusion Flames

H. Bockhorn, M. Charwath, R. Suntz
Institut für Technische Chemie und Polymerchemie
Karlsruher Institut für Technologie (KIT), Germany

The effects of single soot forming processes (particle formation, PAH–condensation, particle coagulation, surface growth, and soot oxidation) on soot particle properties are analyzed. In combination with measured data of stationary methane/air- and acetylene/air-diffusion flames obtained using a 2-colour TIRE-LII technique, the dynamic behavior of a particle-ensemble along streamlines is studied by numerical simulation. The applied numerical method covers the calculation of soot particle properties based on the species mole fractions of the gas phase chemistry (>100 different chemical species) for a detailed kinetic mechanism (including 532 reactions).

Introduction

To predict soot formation during combustion it is indispensable to validate the chosen numerical model. No matter which kind of soot formation model (empirical and semi-empirical models, models based on a detailed gas phase chemistry) is used, it is always preferable to have access to an experimental data base which includes besides absolute reference values (e.g. local f_V, N_T, etc.) also information about the local dominating soot forming process. In this way any local discrepancies between simulated and experimental data can be lead back to a specific process which in turn helps to improve the existing model. This is of particular interest if a detailed chemistry soot formation model with several source terms of soot formation is applied.

In this study, it is shown how the dominating soot formation process can be identified along a streamline in a laminar steady–state diffusion flame. On the one hand, this analysis is based on a general discussion of the effects of a single soot forming process on soot particle properties. On the other hand, it is based on measured data obtained using a 2-colour TIRE-LII technique [1]. By comparing methane/air- with acetylene/air-diffusion flames, it can be seen that the evolution of the dominating processes along a stream line is different which results in different local soot particle properties. Especially with respect to the evolution of the particle size distribution characteristic, a different behavior can be observed.

Results

The analysis of the dominating particle soot formation process along a streamline is performed in simulated methane/air-diffusion flames. Based on the species mole fractions of the gas phase chemistry (>100 different chemical species) for a detailed kinetic mechanism (including 532 reactions), soot particle properties (f_V, N_T, r_m) are calculated as a gas-to-particle process. The comparison of simulated and experimental data shows that the evolution of dominating soot forming processes along a streamline as well as the soot volume fractions and the particle number densities agree quite well.

With respect to the oscillating flame the focus is drawn on the temporal evolution of soot particle properties. The oscillation of the flame is induced by a periodical modulation of the fuel flow with frequency of f_{exc}= 10 Hz. The measurements show that the temporal evolution of the soot volume fraction in the oscillating flame is non-linearly coupled with the temporal evolution of the excitation. Moreover, the time averaged soot concentration of the oscillating flame is increased by a factor of 1.3 compared to a stationary flame with an equivalent mean fuel flow rate.

By comparing soot particle properties of the oscillating flame with those of a fuel flow equivalent stationary flame, it can be seen that the oscillating flame can't be represented by a temporal sequence of stationary flames. By means of the introduced numerical method the non-linear coupling of the soot volume fraction and excitation can be predicted and is primarily caused by the time–varying flow field. However, the experimental finding of an increased time–averaged soot concentration of the oscillating flame can’t be predicted. This clearly indicates that soot formation for the given time-varying boundary conditions differs from the soot formation of stationary boundary conditions. Thus, the oscillating flame can’t be simulated by means of a soot model which relies on stationary boundary conditions.

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