Evidence of Nucleation Flames: A Valuable Tool for the Study of Soot Particles Inception

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Abstract
In this paper, we discuss the possibilities of stabilising “nucleation” flames, that is, rich flames generating soot particles for which surface growth processes are not observed. The experimental conditions for these flames are in this work determined by laser induced incandescence (LII) measurements. We also report the concentration profiles of naphthalene and two mass isomers, the pyrene and fluoranthene, measured by jet cooled laser induced fluorescence (JCLIF) in both “standard” sooting flame (with soot growth) and in a nucleation flame. From the following discussion, we highlight the interest of using this kind of flame as a valuable tool for the comprehension of the soot particles inception.

Introduction
The understanding of soot formation mechanisms in flames, and more specifically the nucleation process, is still under debate. To deal with this crucial step, low pressure laminar flames are particularly well suited because of the large reaction zone provided by the low pressure which offers the ability to spatially resolve the very early soot formation zone. The number of soot particles is however much lower than at atmospheric pressure which requires therefore sensitive techniques to be implemented in order to get accurate data.

This work presents some results of the study we carried out on the formation of soot particles in premixed CH₄/O₂/N₂ flames done by jet cooled laser induced fluorescence (JCLIF) and laser induced incandescence (LII). Flames were stabilised at 26.6 kPa (200 torr). In this paper, we report the experiments we make for two different equivalence ratios (Φ = 1.95 and 2.32). Φ = 1.95 corresponds to the equivalence ratio for which LII signals begin to be measurable along the flame.

We specifically took advantage of the low-pressure conditions to probe with a good spatial resolution the soot inception zone of the flames. Mole fraction profiles of three PAHs including naphthalene and two mass isomers, pyrene and fluoranthene, have been determined in these flames. Significant differences between the evolution of the profiles of the Φ = 1.95 flame and the Φ = 2.32 are observed. The evolution of the intensity of the LII signals with the laser energy (fluence curves) is reported for different heights above the burner (HAB).

As discussed in the following, these experiments highlight the possibilities of generating nucleation flames, that is, flames which generate particles experiencing only very weak or even no surface growth.

1. Experiment Setup

1.1 Flame apparatus
The flat-flame burner (6 cm diameter) we used, provided by Holthuis & Associates, has been described previously [1,2]. Measurements of PAHs and soot particles have been carried out in different methane flames diluted with nitrogen. The flame conditions are reported in table 1. All these flames were considered as sooting flames featuring a yellow colour characteristic of the soot particles.

<table>
<thead>
<tr>
<th>Φ</th>
<th>1.95</th>
<th>2.05</th>
<th>2.15</th>
<th>2.32</th>
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<tr>
<td>C/O</td>
<td>0.49</td>
<td>0.51</td>
<td>0.54</td>
<td>0.58</td>
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<td>X₇₅CH₄</td>
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<td>43.0%</td>
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<td>43.5%</td>
<td>42.0%</td>
<td>41.4%</td>
<td>39.8%</td>
</tr>
<tr>
<td>X₇₅N₂</td>
<td>14.0%</td>
<td>15.0%</td>
<td>14.0%</td>
<td>14.0%</td>
</tr>
</tbody>
</table>

Table 1: Flames conditions

1.2 LII Setup
A schematic of the LII setup is reported in fig.1.

Figure 1: Experimental LII Setup

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LII experiments were carried out directly inside the flame by using a Nd:YAG laser (Quantel 781C) to heat the soot particles [3]. The radial irradiance profile of the beam has been transformed into a top hat energy profile by the use of a rectangular slit (0.7mm x 2.3mm) and a converging lens (f=1 m). The energy of the laser beam could be adjusted thanks to an optical attenuator and was monitored with a power meter after the output window. Reflective losses were taken in account. LII signals were recorded at 90° from the incident beam thanks to a two-achromatic-lenses collecting system. The vertical spatial resolution of the LII measurements inside the flame was achieved with a horizontal slit (0.1mm x 0.5mm) parallel with the laser beam and placed in front of a UV-visible PMT (photons XP 2020Q, spectral range 150–650 nm and maximum sensitivity around 420 nm). Signals from the PMT were acquired and digitized by an oscilloscope (Lecroy WaveRunner 6050, 500MHz bandwidth, 5GS/s sampling rate).

1.3 JCLIF Setup

A schematic representation of the setup is reported in fig.2.

![Figure 2: Experimental JCLIF Setup](image)

JCLIF experiments were carried out after the sampling of the species from the flame thanks to an axially-oriented microprobe which was a thin quartz tube (6 mm diameter) ended by a 20° conical aperture with a diameter of 300 µm. Then species are directly cooled down in the expanded free jet generated inside the analysis chamber. LIF measurements were done directly in the free jet in this low pressure chamber. By this way, spectra of sampling PAHs highlight specific spectral structures which enable their selective measurement by LIF. In the absence of collision inside the free jet, LIF signal can be calibrated by studying the LIF signal issued from pure compounds with known concentrations sent and cooled down inside the free jet.

The laser system we used consisted of a Quantel Nd:YAG laser, pumping a dye laser (TDL70 Quantel) with the 2nd harmonic at 532 nm. Tuneable wavelengths covering different spectral ranges could be generated by using different dyes to match the spectral excitation range of the three studied PAHs. The laser beam was spatially reduced to a diameter of approximately 2 mm with a pinhole and sent into the analysis chamber, slightly focused with a converging lens (500 nm focal lens). The laser energy was adjusted around 0.012-0.024 J/cm² to be in the linear regime of fluorescence. Fluorescence emission spectra were recorded via a spectrometer Acton 2500i, equipped with a 300 gr/mm grating, which could be either coupled to a 16 bit intensified CCD camera (Roper Pimax II) or to the photomultiplier (Photonis XP2020Q) described previously. The conditions of excitation and collection wavelengths for the measurement of the different PAHs are reported in table 2.

<table>
<thead>
<tr>
<th></th>
<th>Naphthalene</th>
<th>Pyrene</th>
<th>Fluoranthene</th>
</tr>
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<td>Transition</td>
<td>S\textsubscript{ex}-S\textsubscript{0}</td>
<td>S\textsubscript{ex}-S\textsubscript{0}</td>
<td>S\textsubscript{ex}-S\textsubscript{0}</td>
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<td>λ\textsubscript{ex}=307.6 nm</td>
<td>λ\textsubscript{ex}=321 nm</td>
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<tr>
<td>Collection</td>
<td>320&lt;λ\textsubscript{c}&lt;340</td>
<td>370&lt;λ\textsubscript{c}&lt;390</td>
<td>430&lt;λ\textsubscript{c}&lt;450</td>
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</table>

Table 2: Spectroscopic data

2. Results and discussion

LII experiments have been carried out in the two different equivalence ratio flames defined in table 1. As discussed in details in a recent review [4], the LII emission intensity is defined as $I_{\text{LII}} = K_T^\text{eff} B(T,\lambda)w_{\text{laser}}$, where $B(T,\lambda)$ is the Planck function, $w_{\text{laser}}$ is the width of the laser sheet, and $K_T^\text{eff}$ is defined as the absorption coefficient $K_T^\text{eff} = N_p\pi^2d_p^2E(m_\lambda)/\lambda$, where $N_p$ is the number density of primary particles, $d_p$ the soot particle diameter, $\lambda$ is the measurement wavelength and $E(m_\lambda)$ is a light absorption function of the complex refractive index of soot $m_\lambda$. $K_T^\text{eff}$ scales linearly with $f_s$, as $f_s = K_T^\text{eff}/(6\pi E(m_\lambda))$ and the rate of signal decay scales with the active area for conductive cooling which correlates with $d_p$ [5]. In fig.3 are reported the evolution of the temporal LII signals we measured for different heights above the burner for the two different equivalence ratios.

In the richest flame, we can deduce from these experiments that the LII signal can be correlated to three different regions. A first region, ranging from 11 to 16 mm corresponding to a zone where the temporal LII decays do not evolve with the height above the burner. We therefore assign this area to the nucleation zone of the flame. After this zone, we clearly observe an increase of the temporal decays of the LII signal, from 16 to 36 mm. These measurements gives thus evidence of a growing zone of the soot in this part of the flame, where coalescence and coagulation processes as well as surface reactions could take place. Finally, we can define a last region from 36 up to 44 mm above the burner, where the temporal LII decay curves do not
that these nascent particles could not be sublimated even at the highest available laser energies.

The evolution of the shape of the fluence curves denotes therefore a sensible evolution of the light absorption function $E(m_3)$ according to the height above the burner correlated with the evolution of the physicochemical properties of the soot particles according during the soot formation process. This last point is coherent with the fact that nascent soot are expected to highlight different optical properties from those of mature soot.

Concerning the $\phi = 1.95$ flame whose experiments are reported in fig.4.b, we denote very similar shape of fluence curves for whatever the heights above the burner, characterised by a quasi-linear dependence with the laser energy. We also remark that the particles in this flame could not reach the sublimation threshold for any height above the burner as it was the case in the nucleation region of the $\phi = 2.32$ flame. Very interestingly, the value of the slope characterising the linear fluence curves in the nucleation zone of the richest flame is the same as the one we obtain in the $\phi = 1.95$ flame.

Therefore, we denote a strong similarity between the response to the laser heating of the soot particles formed in the $\phi = 1.95$ flame and in the nucleation region of the $\phi = 2.32$ flame. This comparison clearly indicate some similarities of the physicochemical properties of the nascent soot of the richest flame with the soot of the $\phi = 1.95$ which lead us to consider this last flame as a nucleation flame, i.e., a flame where only nucleation processes take place. Note that this kind of flame is not fuel dependent and can also be stabilised at atmospheric pressure. We have recently reported in a paper a study concerning a nucleation ethylene/air flame stabilised at
The maximum concentrations of PAHs. For the region of the soot particles appears just after the peak of aggregation. Formation processes, i.e. nucleation, surface growth, correspond to the three different steps of the soot has been plotted in both figures 5 and 6. They according to the LII temporal decays measurements have been calibrated in soot volume fraction profile different PAHs in both flames. Note that LII profiles of naphthalene, pyrene and fluoranthene and soot volume fraction profiles we obtained are reported in fig.5 for the \( \phi = 2.32 \) flame and fig.6 for the \( \phi = 1.95 \) flame.

We observe that, in both flames, the nucleation flame, we have also recorded the mole fraction profiles of soot particles as well as three different PAHs in both flames. Note that LII profiles have been calibrated in soot volume fraction profile thanks to extinction measurements carried out by cavity ring down spectroscopy (CRDS) [7]. Mole fraction profiles of naphthalene, pyrene and fluoranthene and soot volume fraction profiles we obtained are reported in fig.5 for the \( \phi = 2.32 \) flame and fig.6 for the \( \phi = 1.95 \) flame. Figure 5: Mole fraction profiles PAHs and soot volume fraction profiles measured in the \( \phi = 2.32 \) flame.

Concerning the \( \phi = 1.95 \) flame, we assign its whole area as a nucleation region, which is reported in fig.6, as we did not observe any evidence of soot growth in this flame according to the LII experiments. We can first note the shape of the PAHs profiles is very different from the ones determined in the \( \phi = 2.32 \) flame. Especially pyrene and fluoranthene profiles do not highlight any strong re-increase of concentration in the burnt gases but are characterised by a barely constant value following an initial increase of concentration before the soot inception. Again, we observe a good correlation between the beginning of the soot formation and the peak of the PAHs concentration profiles. The soot mole fraction profile is characterised by a continuous increase all along the flame, but we do not observe any evident break of slope as it was the case for the growing zone defined in the \( \phi = 2.32 \) flame.

An interesting point regarding these experiments is the similarity of the evolution of the pyrene and...
fluoranthene profiles in the nucleation region between the two flames. Indeed, one can note that the concentration profiles of these compounds measured in the $\phi = 1.95$ flame appears as an enlargement of the concentration profiles of the same species measured in the nucleation region of the $\phi = 2.32$ flame. The concentration profiles in both cases are characterised by a quasi-stationary state meaning that reactions of consumption and formation of these species balance each other in this part of the flames. This observation is to be explored more deeply, especially because we have not yet measured the temperature profiles for these flames which can be of importance to explain the shape of these profiles.

The soot volume fraction profiles increase all along the flame in both cases. From the definition of $f_v$ given in section 3, the increase of the soot mole fraction can be related to the increase of the soot number particles and the soot diameter. Concerning the $\phi = 1.95$ flame, we showed, from the determination of the temporal LII decay signals and the corresponding fluence curves that there was no diameter increase all along the flame height. Therefore, the increase of the soot volume fraction in this flame can only be related to the increase of the number of particles due to the nucleation process. By comparison, in the $\phi = 2.32$ flame, the soot increase may be mainly attributed to the soot growth as shown in [3].

Regarding all these points, this flame, we defined as a "nucleation" flame, could certainly be of great interest for the study of the nucleation process which currently is the main grey area for the comprehension of the soot formation processes. This kind of flame, characterised by the absence of any surface growth reactions or growing processes as coagulation or coalescence, allows great simplification for the development of soot formation models. The parameter $\alpha$ corresponding to the fraction of reactive soot surface available for reactions, which is a difficult parameter to estimate, can be neglected here as there is no need to care about the growth of particles by surface reactions as the increase of the soot concentration is only due the increase of the number of particles. Hence, all these simplifications provide some evident facilities that could really profit to the developments of soot models and more specifically the understanding of the nucleation process.

3. Conclusion

In this work we have reported evidences of the existence of nucleation flames, which are rich flames characterised by the formation of soot particles which are not subject to growth processes. Concentration profiles of three different PAHs and corresponding soot volume fraction have been reported in two different flame, a reference flame ($\phi = 2.32$) and the so called nucleation flame ($\phi = 1.95$).

Concerning the PAHS, although we did not measure yet the temperature profiles, they seem to be well correlated to the different nature of the flames. All PAHs profiles are characterised by maximum values just before the beginning of the inception of soot particles. Moreover, the shape of the pyrene and fluoranthene profiles, which are potentially PAHs that could be responsible of the nucleation, are characterised by a quasi-stationary state indicating an equilibrium between the formation and consumption reaction rates both in the nucleation region of the $\phi = 2.32$ flame and in the nucleation flame.

Finally, different experiments have been carried out by LII in order to characterise the soot particles. From these experiments, it appears that in both flames, we observe a growing of the soot mole fraction $f_v$ with the height above the burner. However, the growing of $f_v$ in the nucleation flame has been shown to be only due to the increase of the number of particles. We believe that this point could represent an important simplification for the development of soot formation model and that nucleation flames could be used as valuable tools for experimental and modelling studies with the aim of elucidating the soot nucleation processes.

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References: