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FLAME STRUCTURE 2014
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Abstract

This paper presents some results of the study we carried out on the formation of soot particles in low-pressure premixed $CH_4/O_2/N_2$ flames by jet cooled laser induced fluorescence (JCLIF) and laser induced incandescence (LII). Flames were stabilised at 26.6 kPa (200 torr). Three different equivalence ratios were tested ($\Phi = 1.95$, 2.05 and 2.32), $\Phi = 1.95$ corresponding 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 some PAHs including naphthalene, pyrene and fluoranthene have been determined in these three flames. Significant differences in the evolution of the profiles between the $\Phi = 1.95$ flame and the other ones are observed. The evolution of the LII signals with laser fluence (fluence curve), time (temporal decay) and emission wavelength is reported at different heights above the burner. Also, significant different behaviours of the fluence curves are observed according to the probed region of the flames and Φ. In addition, while the surface growth process is accompanied by an increase in the LII decay-times (indicator of the primary particle diameter) at higher Φ, decay-times become increasingly shorter at lower Φ reaching a constant value along the flame height at $\Phi = 1.95$. These behaviours are consistent with the detection of the smallest incandescent particles in the investigated flames, these particles having experienced very weak surface growth. We therefore have denoted this $\Phi = 1.95$ flame the “nucleation flame” since only nucleation of the particles seems to take place followed by only very weak surface growth processes.

Introduction

The work reported in this paper follows up previous studies made in similar low-pressure methane flames in which several mole fraction profiles of soot precursors like naphthalene and pyrene [1, 2] were measured by jet-cooled laser-induced fluorescence (JCLIF). Peak mole fraction of aromatic compounds was found to increase significantly with Φ and p, the dependence of which is increasing with the size of the aromatics. Concerning the measurements of the soot particles we report in this previous paper that the variation of the LII signal with laser fluence (LII fluence curve) showed an important dependence with the height above the burner (HAB) already observed in atmospheric premixed flames [3] but smaller. These results indicate that the response of the particle to the laser fluence depends on soot maturity leading to difficulties to establish the relationship between the LII signal and the soot volume fraction [4]. In addition spectral variations of the soot absorption function E(m) (m being the soot refractive index) have been reported in premixed atmospheric flames [5], while at low pressure, the ratio of the soot absorption functions at two different wavelengths E(m 532 nm)/E(m 1064 nm) was found to decrease significantly in the early soot formation zone [6]. In atmospheric pressure premixed flames, variations of E(m) with HAB have also been pointed out [5, 7]. These results could be the fact of drastic changes in the nature of the incandescent molecular entities according to the step of the soot formation.

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Approach

In order to deepen these studies, we have carried out a series of experiments by using both the JCLIF and the LII method (1064 nm excitation) to detect PAHs and soot particles in low-pressure premixed flames ($CH_4/O_2/N_2$) stabilised at 26.66 kPa with different Φ. Concerning the JCLIF method, we significantly refined the sampling of the species and improved the optical detection setup in order to increase the sensitivity. By this way, we succeeded in measuring quantitative profiles of naphthalene and pyrene even in the $\Phi = 1.95$ flame. Moreover we took advantage of this spectroscopic method to measure fluoranthene, which is an isomeric form of pyrene, assumed to play a role in the soot nucleation processes [8-11]. However, this compound is difficult to be measured by mass spectrometry and usually neglected, the mass 202 amu being often attributed to pyrene only.
In these flames, the relative weight of the soot growth process and of the nucleation is expected to vary. By contrast to the work reported in [12], the radial laser beam profile was transformed into a top-hat beam for LII experiments insuring a nearly constant heating of the soot particles contained in the collection volume and facilitating the interpretation of the signals behaviour. In the present work, the LII fluence curves and the LII temporal decays were measured along all the investigated flames, i.e., at different stages of the soot formation from the nucleation zone to the burnt gases and at different Φ. Furthermore, emission spectra subsequent to the laser heating of the particles were recorded. Assuming blackbody radiation behaviour, the temperature of the laser-heated soot particles could be estimated along with their formation. The behaviour of the LII signal with the laser fluence indicates an important change of the LII response with flame conditions, i.e., with soot maturity. In addition, the characteristics of the first measurable incandescent particles in terms of LII response and LII decay-time were determined showing that LII technique is sensitive enough to detect very small nanoparticles.

Result and discussion

Naphthalene, pyrene and fluoranthene profiles have been quantitatively determined in the three flames by JCLIF. In the two richer flames, naphthalene and pyrene mole fraction profiles highlight the same kind of shape which can be separated into 3 different regions, each associated with a different chemical process. A first zone where only gaseous reactions take place leading to the rapid formation of these compounds. This zone corresponds approximately to the region near the burner surface up to 10 mm. Then a second zone where the PAHs are consumed up to a minimum threshold. This zone and is located between 10 and 20 mm above the burner and corresponds to the region of the flame where soot are formed and begin to grow essentially by heterogeneous reactions at the surface of the soot with C_2H_2 and some PAHs [8]. This behaviour could suggest that these species would be implicated in some heterogeneous reactions at the surface of growth particle. Finally there is

a third region, which can be regarded as a pyrolysis reaction zone where the PAHs mole fraction continuously increases with height above the burner. In the Φ=1.95 flame, i.e. the "nucleation" flame characterised by the absence of growth of the particles, there is a significant difference in the shape of the pyrene profile in comparison with the two other flames (2.32 and 2.05). We do not observe any reduction of the pyrene concentration in the region after 10 mm. There is no peak anymore but a plateau which appears around 8 mm until 20 mm before a re-increase of the concentration of the pyrene in the burnt gases. This shape could be related to the absence of heterogeneous reactions between soot and pyrene in the "nucleation flame". Concerning the fluoranthene, the three measured mole fraction profiles highlight all the same shape consisting of a fast increase followed by a plateau from 10 to 20 mm and finally a re-increase of the concentration in the burnt gases. Its concentration in the plateau appears to be around one quarter of the pyrene mole fraction, a contribution which has to be taken into account when measuring pyrene using mass spectrometry for instance.
The LII response to laser fluence (fluence curve) has been measured at different HAB in the flames. These results have been completed by time-resolved LII measurements for monitoring the evolution of particle diameter. The flames have been selected for their different contributions of the soot nucleation process relatively to the surface growth one. That possibility is facilitated by the very high sensitivity of soot formation to Φ in low-pressure flames. At Φ = 2.32, a continuous increase in the LII decay-times (measured at 1/e of the peak LII signal) is observed with HAB, in accordance with soot growth process. Decreasing Φ leads to reduce the soot growth until disappearance at Φ = 1.95. Globally, the decay-times at the lowest HAB in each flame tend towards a same value around 21 ns. This short decay-time results from the cooling of very small nanoparticles. Concomitantly, fluence curves exhibit significant variations with Φ never reported before, while weaker variations with HAB were observed at atmospheric pressure [3]. Particularly, the typical shape of the fluence curves in three phases, consisting of a LII increase above a fluence threshold before reaching a plateau followed by a decrease due to sublimation, is well observed for mature soot particles at high HAB in the Φ = 2.32 flame. However, this shape gradually changes when decreasing Φ to move towards a nearly linear behaviour at low HAB and all along the Φ = 1.95 flame. The blackbody feature of the incandescent particles present in the flames was satisfactorily checked from spectrally resolved LII measurements on a large range of HAB. Hence, we conclude that the LII characteristics at low HAB are due to the smallest incandescent particles present in the investigated flames which are thought to be a product of the nucleation process induced by collision of some gaseous PAHs. Smaller particles if they exist do not incandesce. The particle diameter in the nucleation flame has recently been estimated to be around 1 nm [13] using a model for LII developed by the Lund group.

Conclusion

The observed variations of the LII response are probably due to important changes of the particle properties in terms of soot absorption

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function, density, heat capacity in the inception zone of the flames where the smallest particles exist. They could be highlighted in this work thanks to the large width of the inception zone in low-pressure conditions. These variations complicate the interpretation of the LII signals in terms of soot volume fraction. The sensitivity of LII was shown high enough to probe the smallest incandescent particles in our flames. LII was found very relevant to define the flame characteristics ($\Phi = 1.95$, 26.6 kPa) in which particles are mainly formed by nucleation. In these conditions, it is expected that α would tend to zero. This perspective, combined with the measurement of the volume fraction profile of the incandescent particles and of large PAHs, is very attractive to clarify the nucleation step in the soot formation process.

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