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Hydrogen as a fuel additive in laminar premixed methane flames: Impact on the nucleation and growth of soot particles

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1 **Hydrogen as a fuel additive in laminar premixed methane**
2 **flames: Impact on the nucleation and growth of soot**
3 **particles**

4
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10 **Full-Length Article**

11
12
13 **Supplemental Material (SM) is available:**

14 SM1: Additional information (PDF file)

15 SM2: Experimental data (Excel file)

16
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29 **Abstract:**

30 This work reports new experimental data regarding the impact of H₂ on slightly sooting
31 methane flames ($\Phi=1.91$) characterized by the formation of soot particles undergoing growth
32 processes. This study has been carried out in three atmospheric sooting premixed methane
33 flames with added H₂ (2% of the total flowrate) or substituted (10% molar comparing to CH₄
34 fuel).

35 The mole fraction profiles of selected aliphatic and aromatic compounds (C₁-C₁₆) have
36 been measured by Gas Chromatography and Jet-Cooled Laser-Induced Fluorescence.
37 Concerning the soot particles, we have implemented for the first time an analytical methodology
38 based on in-situ measurements by Laser-induced Incandescence and Cavity Ring-Down
39 Spectroscopy coupled with ex-situ measurements by Scanning Mobility Particle Sizing
40 (SMPS). This original approach allows to determine the soot volume fraction profiles and
41 corresponding evolution of the particle number densities and particles size density function
42 without requiring accurate knowledge of the dilution ratio during SMSP measurements.

43 The reported data highlight that the introduction of H₂ strongly influences the formation
44 of aromatic species and soot depending on the operating conditions (H₂ addition or
45 substitution). The impact of H₂ was evaluated on the nucleation step and the soot growth
46 processes. In that context, we notably show that the H₂ substitution inhibits while the H₂
47 addition favors the formation of nascent soot particles, and furthermore the H₂ addition
48 generates substantial modifications in the dynamic of the soot growth processes. This work also
49 supports the idea that the onset of the particle nucleation might be controlled by specific
50 concentration thresholds of aromatic precursors.

51 **Keywords:** soot, hydrogen, polycyclic aromatic hydrocarbons (PAHs), soot growth, premixed
52 flame

53 1. Introduction

54 Reducing the emissions of soot and gaseous pollutants from the combustion of
55 conventional hydrocarbon fuels is an ongoing challenge. Hydrogen (H₂) is well-known as a
56 zero-carbon energy carrier with low ignition energy and high burning velocity [1–3]. However,
57 the use of H₂ alone in real industrial systems is not yet optimal due to certain inherent handling
58 difficulties and the necessary adaptations of industrial processes. Major safety issues arise from
59 the wide flammability range and low ignition energy of H₂ [4–6]. In this context, H₂-
60 hydrocarbon blends, which are easier to implement in real combustion systems, have received
61 increased attention due to different positive aspects notably related to their increased
62 combustion efficiency and propensity to reduce soot and gaseous pollutant emissions. The local
63 flame extinction, combustion stability and power output of CH₄ combustion have all been
64 shown to be improved by H₂ enrichment [7,8], and the addition of small amounts of H₂ to
65 methane has been demonstrated to increase the performances of gas powered spark-ignited
66 engines [9]. Moreover, the presence of H₂ in synthetic natural gas flame has been shown to
67 inhibit the formation of CO and CO₂ [10].

68 The impact of H₂ on the formation of soot precursors and soot particles has also been
69 the subject of numerous experimental and modeling studies [11–35]. Regarding soot precursors,
70 the impact of added H₂ (40% in CH₄) in a methane laminar premixed sooting flame
71 (equivalence ratio relative to CH₄ $\Phi_C=2.2$) has notably been shown to enhance the formation of
72 aliphatic C₁-C₄ species as well as benzene and toluene [29]. Ezenwajiaku et al. [28]
73 experimentally studied the impact of H₂ (20% in CH₄) on the formation of polycyclic aromatic
74 hydrocarbons (PAHs) in a diffusion flame and concluded that H₂ addition to fuel decreased
75 their concentration.

76 Haynes et al. [25] found that H₂ addition (3% of total flame flowrate) to an ethylene
77 flame operating at the soot inception C/O ratio promoted the formation of nascent soot. By

78 contrast, Liu et *al.* [30] and Xu et *al.* [31] investigated the effect of H₂ addition (up to 40%
79 comparing to the base fuel) on soot formation in methane diffusion flames and found that the
80 addition of H₂ in these cases strongly decreased the soot volume fraction. This tendency to
81 decreasing the soot volume fraction in flames when adding amounts of H₂ (from 10 up to 50%
82 H₂/fuel) has been observed in numerous works investigating flames stabilized with various
83 fuels as ethane, ethylene, propane, butane [15,17,21,22,24,36,37].

84 Besides, De Iuliis et *al.* showed that the introduction of H₂ in an ethylene/air premixed
85 flame [24] by a substitution procedure slowed down the soot growth process due to the decrease
86 of the H/H₂ ratio. Choi et *al.* [16] investigated the effect of H₂ addition on the micro- and nano-
87 structure of soot particles in an ethylene/air counter-diffusion flame. They highlighted that H₂
88 addition decreased the size of the soot microstructures and enhanced the formation of PAHs
89 containing 5 carbon atom rings that induce the curvatures into the carbon lamella.

90 The effect of H₂ on the number density of soot particles has also been investigated in
91 literature. Tesner et *al.* [14] found that H₂ addition (30% comparing to fuel) to a methane
92 diffusion flame increased the number density of soot particles. Zhao et *al.* [22] mentioned that
93 H₂ addition (20% comparing to fuel) and H₂ substitution (25% of ethylene by H₂) to an ethylene
94 laminar diffusion flame decreased the number density of soot particles by 23% and 66%
95 respectively, comparing to the reference flame. However, the H₂ effect was not only due to the
96 dilution and chemical inhibition but also to the reduced number of carbon atoms in the initial
97 mixture.

98 Hence, at the state of the art, the literature shows that the introduction of H₂ into sooting
99 flames enhances or inhibits the formation of soot particles and their precursors depending on
100 the operating conditions. We recently also showed that the introduction of H₂ in a nucleation
101 methane flame ($\Phi_C=1.82$), i.e. a flame generating only nascent soot particles [32], drastically
102 reduced or enhanced the formation of aromatic species and the soot volume fraction, depending

103 on the way of introducing H₂ (either by addition or substitution to the diluent). However, these
104 flames did not allow studying the soot growth process and the impact of H₂ on the soot particles
105 distribution and soot number density.

106 In the present work, as part of a continuing effort to improve the understanding of the
107 impact of H₂ on soot formation, we investigated the impact of H₂ on a slightly richer methane
108 flame ($\Phi_C=1.91$) characterized by the formation of soot particles undergoing growth processes.
109 As demonstrated by [38], both nucleation and growth process happen simultaneously under
110 fuel-rich flame conditions. These richer operating conditions allowed us to examine the effect
111 of H₂ on both the nucleation and growth processes.

112 Similarly to our previous work [32], we employed two different approaches to introduce
113 H₂ to the reference methane flame, consisting either in keeping constant (H₂ substitution) or
114 slightly increasing (H₂ addition) the total gas flow rate. We implemented a large panel of
115 experimental methods to record the most complete set of experimental data to gather
116 information on the role of H₂ on these two specific soot formation steps. Hence, we measured
117 the mole fraction profiles of gaseous species including selected aliphatic and aromatic
118 compounds (C₁-C₁₆) in the different flames. Moreover, we determined the soot volume fraction
119 profiles as well as the corresponding evolution of the soot particle size distribution and number
120 density using a combination of complementary highly sensitive analytical tools. To this aim,
121 we developed a new analytical method based on the coupling of laser induced incandescence
122 (LII), cavity ring-down spectroscopy (CRDS) and scanning mobility particle sizing (SMPS) to
123 determine the soot number density from the soot volume fraction and soot particle size
124 distribution measured in the flame.

125

126 **2. Experiment methods**

127 **2.1. Burner and flame conditions**

128 Three atmospheric methane premixed flames were stabilized on a water-cooled
129 McKenna burner equipped with a bronze porous disk (6 cm diameter). The system was already
130 described previously [32]. In the present study, the water in the cooling circuit was kept at
131 296 K and a shield nitrogen flow, introduced in the co-annular section of the porous disk, was
132 set to 1440 NLPH (normal liter per hour) to prevent perturbations induced by the surrounding
133 air.

134 As recently reported for nucleation flames [32], two different approaches have been
135 used to introduce H₂ into the reference methane flame, consisting on either keeping constant or
136 slightly increasing the total gas flow rate. The first method consisted of replacing a small
137 amount of dilution nitrogen, equal to 10% of CH₄ flow rate with H₂, hence preserving a total
138 constant flowrate. The corresponding flame is denoted Φ -1.91_H₂-S. The second method
139 consisted of adding the same amount of H₂ directly to the cold gas supply, therefore leading to
140 a slight increase (around 2%) of the total flowrate compared to the reference flame. The
141 corresponding flame is denoted Φ -1.91_H₂-A. The introduction of such a small quantity of H₂
142 (< 2%) strongly limits its impact on the flame temperature which is an essential parameter in
143 the soot particle formation processes. The experimental conditions of the flames are reported
144 in Table 1.

145

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| | Flame | | |
|--|--------------|--------------------------------|--------------------------------|
| | Φ -1.91 | Φ -1.91_H ₂ -S | Φ -1.91_H ₂ -A |
| Φ_C | 1.91 | 1.91 | 1.91 |
| Φ_{C+H} | 1.91 | 1.96 | 1.96 |
| C/O | 0.479 | 0.479 | 0.479 |
| Total flow rate (NLPH) | 690.6 | 690.1 | 704.5 |
| x_{CH_4} | 0.202 | 0.202 | 0.198 |
| x_{O_2} | 0.211 | 0.211 | 0.207 |
| x_{N_2} | 0.587 | 0.567 | 0.575 |
| x_{H_2} | 0 | 0.020 | 0.020 |
| $T_{adiabatic}$ (K) | 1806 | 1806 | 1787 |
| $T_{uncorrected}$ (K) | 1552 | 1569 | 1543 |
| Flame velocities at 298 K and 1 atm (cm/s) | 9.1 | 9.9 | 9.2 |

153 **Table 1.** Experimental conditions. Flame name: Φ -1.91: CH₄ flame; Φ -1.91_H₂-S: CH₄ substituted-H₂
154 flame; Φ -1.91_H₂-A: CH₄ added-H₂ flame. $T_{adiabatic}$: adiabatic temperature calculated using GASEQ
155 program [39]. $T_{uncorrected}$: measured temperature by using a type B thermocouple without radiative heat
156 loss correction. Flame velocities have been calculated using the GRI mechanism [40]. $\Phi_C = 2 x_{CH_4} / x_{O_2}$
157 and $\Phi_{C+H} = 2 x_{CH_4} / x_{O_2} + 0.5 x_{H_2} / x_{O_2}$

158

159 2.2. Experimental setup

160 In this work, several experiments were implemented to measure the flame temperature,
161 the mole fraction profiles of combustion products (CO, CO₂, H₂, H₂O), aliphatic species (C₁-
162 C₆), benzene, naphthalene, pyrene, soot volume fractions, number density of particles as well
163 as particles size density functions (PSDFs) along the flame height.

164

165 2.2.1. Flame temperature measurement

166 The temperature profiles of the three studied flames were measured with a Pt/Rh(6%)-
167 Pt/Rh(30%) type B thermocouple (diameter 100 μ m) along the centerline of the flame as a
168 function of the height above the burner (HAB) from 0 mm to 16 mm. The thermocouple was
169 coated with a ceramic layer of BeO-Y₂O₃ to reduce catalytic effects [41]. As the main objective
170 of this measure was only to check whether the temperature profile was modified by the H₂

171 addition/substitution, no specific correction has been applied to the reported temperature
172 profiles.

173

174 **2.2.2. Measurement of gaseous species by GC, JCLIF and FTIR**

175 The gaseous species formed in the sooting flames were extracted by a quartz sampling
176 microprobe (350 μm orifice). As described in our previous work [32], gas chromatography
177 (GC) was used to identify and quantify CO, H₂, aliphatic species and benzene. The uncertainty
178 on the mole fraction of gaseous species measured by GC in this study is estimated to be < 5%
179 for major species and < 10% for minor species. Naphthalene and pyrene concentration profiles
180 were determined by jet cooled laser induced fluorescence (JCLIF) while CO₂ and H₂O were
181 measured by Fourier-transform infrared spectroscopy (FTIR). The measurement uncertainty on
182 all these species was estimated < 13%. The C, O and H atomic balances of the three studied
183 flames were found to be close to 100% as detailed in Table S1 of the Supplemental Material 1
184 (SM1).

185

186 **2.2.3. Determination of the soot volume fraction profiles by LII and CRDS**

187 Soot volume fraction profiles were determined by laser induced incandescence (LII)
188 measurements calibrated by cavity ring-down spectroscopy (CRDS) according to a procedure
189 already described in previous papers from our group [32,42]. The same method has been
190 employed and adapted to the present work. Hence, only the main details of the setup will be
191 given here.

192 CRDS experiments were performed by using a Nd:YAG laser (Quantel) generating a
193 laser pulse at 1064 nm. The cavity we used consisted of two identical 25-mm-diameter plano-
194 concave mirrors (radius of curvature: 25 cm) coated to achieve a high reflectivity of
195 $R = 99.96\%$ at 1064nm. The mirrors were separated by distance of 40 cm. The burner was

196 placed at the central position between these two mirrors. A laser pulse was injected inside the
 197 cavity with a specific optical system constituted of two lenses and a pinhole in order to
 198 preferentially match the TEM00 modes of the cavity. The ring-down time characterizing the
 199 lifetime of the laser pulse inside the cavity was recorded thanks to a photomultiplier Hamamatsu
 200 R2257 (PMT). A longpass filter (RG-780) was placed in front of the PMT to limit the parasite
 201 light due to the flame emission. The lifetime of the laser pulse was then transformed into an
 202 extinction value according to a procedure already described elsewhere [32,42]. The measured
 203 extinction coefficient $K_{\text{ext}} = K_{\text{abs}} + K_{\text{sca}}$ (K_{abs} and K_{sca} being respectively the absorption and the
 204 scattering coefficients) was assumed to be equal to K_{abs} (K_{sca} being negligible).

205
 206 LII experiments were also carried out by using 1064 nm laser excitation wavelength
 207 generating by the same laser used for CRDS experiments. The laser beam was expanded into a
 208 collimated horizontal plane using a specific optical system described in details in [32] to provide
 209 a top-hat irradiance profile at the position of the LII collection volume. The LII signal was
 210 collected at right angle of the laser axis by a system of lenses and a Hamamatsu R2257 PMT
 211 positioned behind an entrance slit (0.6 mm vertical \times 6 mm horizontal) and an interference filter
 212 centered at 532 ± 10 nm in order to limit parasite emission and scattering light from the flame.
 213 The LII signals recorded by the PMT were acquired and digitized by an oscilloscope Lecroy
 214 HDO - 4104A.

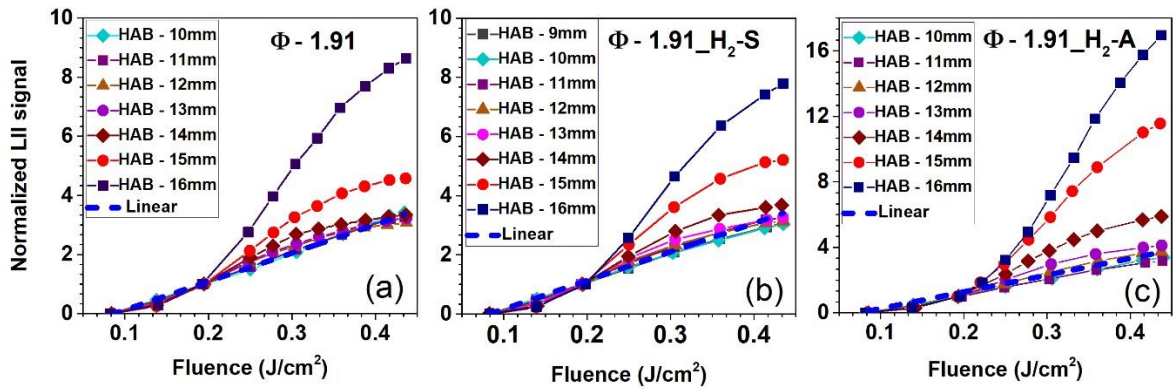
215 Basically, LII signals can be defined according to *Eq.1*:

$$S_{LII}(\lambda_{em}, T_p(t)) = E(m) \frac{48\pi^2 hc^2}{\lambda_{em}^6} \left[\exp\left(\frac{hc}{\lambda_{em} \cdot k_b \cdot T_p(t)}\right) - 1 \right]^{-1} f_v(t) \quad Eq.1$$

216 where $E(m)$ is the absorption function of the particles, T_p the temperature of the heated soot by
 217 the laser pulse, c the speed of light in vacuum, λ_{em} the emission wavelength, k_b the Boltzmann
 218 constant, h the Planck constant and f_v the soot volume fraction.

219 This equation shows a dependence on $E(m)$ and to T_p . In order to determine the LII
 220 profiles representative of the evolution of f_v , it is therefore important to consider the evolution
 221 of the value of $E(m)$ as well as the heated temperature T_p along the flame height. To this aim,
 222 we first determined the fluence curves characterizing the response of the LII signal to laser
 223 energy against the HAB in all studied flames. These fluence curves are reported in Fig.1.

224



225

226 Fig.1: Normalized fluence curves at 0.2 J/cm² obtained in three studied flames. Φ -1.91: CH₄ sooting
 227 reference flame; Φ -1.91_H₂-S: CH₄ substituted-H₂ flame; Φ -1.91_H₂-A: CH₄ added-H₂ flame.

228

229 We arbitrary chose to normalize the LII fluence curves reported in Fig.1 at 0.2 J/cm².
 230 From this figure, it appears that the evolution of the normalized fluence curves with HAB is
 231 relatively similar in the three sooting flames. Hence, we observe that the fluence curves
 232 determined at the lowest heights (HAB ≤ 12 mm), show for the three flames a similar quasi-
 233 linear evolution over the fluence range accessible with our laser. It has been shown that this
 234 behavior is typical of nascent soot particles which are characterized by low $E(m)$ values and
 235 require therefore much higher fluence to reach the sublimation threshold [43,44]. Based on

236 recent characterization of optical properties and fluence curves of such particles [42] we used
237 the constant value $E(m) = 0.250 \pm 0.025$ for the soot particles identified as nascent soot particles
238 in our flames, i.e. for HAB up to 12 mm.

239 At higher HAB, the fluence curves are characterized by a more classical S-shape
240 strongly depending on T_p with an inflexion point appearing around 0.4 J cm^{-2} characteristic of
241 the sublimation threshold of more mature soots [45]. This evolution denotes a change of the
242 optical properties of the detected soot particles correlated with an increase of $E(m)$. The value
243 of $E(m)$ is indeed well known to vary with the soot maturity in flame [46–50]. Values from 0.2
244 to 0.4 are usually considered in the literature to characterize particles from the nucleation step
245 to the fully mature graphite-like particle [51–53]. The determination of the evolution of the
246 $E(m)$ value with soot maturity along the flame height was beyond the scope of this work and
247 has not been carried out. Based on the literature, we rather chose to consider a constant value
248 $E(m)=0.300 \pm 0.030$ as proposed by Yon *et al.* [54] for the more mature soot particles formed
249 from 12.5 mm to 16 mm for all studied flames.

250 All the recorded LII profiles have been measured by using a laser fluence just below the
251 soot sublimation threshold energy determined from these experimental fluence curves to
252 minimize the influence of T_p on the measured LII signal [55]. Based on these considerations,
253 this laser fluence has been defined equal to 0.359 J cm^{-2} for the three flames studied in this
254 work.

255 Finally, LII profiles were calibrated in f_v profiles according to the method already detailed in
256 previous works [32,42] and relying on the measurement of the extinction coefficient K_{ext} carried
257 out by CRDS. This coefficient, defined by the well-known *Eq.2*, has been determined at 16 mm
258 HAB as described in [32,42].

$$K_{ext} = \frac{6\pi E(m)}{\lambda} f_v \quad \text{Eq.2}$$

259

260 Where λ corresponds to the excitation wavelength (1064 nm) used for the extinction
261 measurement.

262

263 **2.2.4 Characterization of the particles size density functions (PSDFs) by SMPS**

264 To measure the particle size distributions, we used a nano-SMPS system (TSI Inc.) as
265 presented in SM1 (Fig. S1) which is capable of measuring size distributions from 1 to 30 nm,
266 coupled to a sampling system based on dilutive microprobe extraction specifically designed for
267 this SMPS experiments.

268 Soot particles were extracted from the flames by using a microprobe made of two co-annular
269 quartz tubes, the outer tube ending with a long thin tip with a 250 μm orifice. This probe was
270 positioned vertically and inserted into the flame throughout the burner stabilization plate. The
271 outer tube was used to send a cold nitrogen flow (6 L min^{-1}) enabling a fast dilution of the
272 sampled material from the flame directly at the entrance of the microprobe. The dilution ratio
273 was estimated in the range 500-3000. The inner tube was connected to a pump system allowing
274 the sampling of the diluted flow of particles from the flame. A 2 L buffer volume interposed
275 between the probe and the nano-SMPS was required to stabilize the pressure in the sampling
276 line. This system has been implemented in order to avoid post-sampling chemical reactions as
277 well as coagulation and/or aggregation of the sampled particles.

278 The polydisperse aerosol was injected in the TSI nano-SMPS consisting, in the order, of:
279 (1) a soft X-ray neutralizer model 3088 to reach a known particle charge distribution function;
280 (2) a differential mobility analyzer (DMA) model 3086 operating over the size range 1-30 nm
281 and controlled by an electrostatic classifier model 3082; (3) a nano-enhancer model 3757 that
282 pre-activates the smallest particles in an environment supersaturated in diethylene glycol, and
283 finally (4) a standard n-butanol condensation particle counter (CPC) model 3570 [56]. To
284 minimize diffusion losses, the highest total flow 2.5 L min^{-1} was used in all experiments and

285 the sampling line was optimized for minimal distance (<2 m) between the probe and the nano-
286 SMPS [57].

287

288 **3. Determination of the profiles of the soot particle number densities**

289 To determine the soot particle number density along the flame HAB, we used an original
290 methodology relying on the coupling of the data obtained by SMPS and LII/CRDS
291 measurements. Basically, the SMPS system was used to determine the normalized PSDFs
292 against HAB for the studied flames. The PSDFs were then calibrated into absolute number
293 densities with the soot volume fraction profiles determined by LII and CRDS, according to the
294 analytical procedure explained below. This procedure provides the advantage of not requiring
295 accurate knowledge of the dilution ratio during SMSP measurements, which remains a strong
296 limitation for ex-situ measurements.

297 It is to be noted that comparisons between f_v deduced from the measurement of the soot
298 PSDFs by SMPS with direct *in situ* extinction measurements have already been reported in the
299 literature and showed very good correlation [58]. The main uncertainty, according to this
300 comparison, has been attributed to the potential variations of the soot refractive index. In our
301 work, the studied flames have been shown to produce soot particles characterized by fluence
302 curves indicating a slight evolution of the optical properties all along the flame height, limiting
303 therefore this issue.

304

305 **3.1. Theory**

306 The particle size distribution function (PSDF) of soot in the flame sampled volume can
307 be expressed as a function of the particle number density N and the particle diameter D_p as:

$$\frac{dN}{d \log D_p} = \sum_{i=1}^2 N_i \left(\frac{dN}{d \log D_p} \right)_i \quad \text{Eq. 3}$$

308 The sum of functions in Eq. 3 is necessary to account for the bimodal structure observed
 309 at some HAB. N_i is the (partial) particle number density of each mode. The total particle number
 310 density is given by:

$$N_{\text{tot}} = \int_0^{\infty} \frac{dN}{d \log D_p} d \log D_p = N_1 + N_2 \quad \text{Eq. 4}$$

311 $\left(\frac{dN}{d \log D_p} \right)_i$ is well represented, as it will become clear in the experimental section, by
 312 lognormal distributions having median diameter $\bar{D}_{p,i}$ and geometric standard deviation $\sigma_{g,i}$ [59–
 313 64]:

$$\left(\frac{dN}{d \log D_p} \right)_i = \frac{1}{\sqrt{2\pi} \log \sigma_{g,i}} \exp \left[-\frac{(\log D_p - \log \bar{D}_{p,i})^2}{2(\log \sigma_{g,i})^2} \right] \quad \text{Eq. 5}$$

314 It is important to notice that in this work we chose the normalized number density $\frac{dN}{d \log D_p}$
 315 over $\frac{dN}{dD_p}$ since the former is independent of the instrument resolution and therefore particularly
 316 useful when intercomparing data from different instruments. In the explored D_p range (1.5–
 317 15 nm), soot particles are spherical and isolated [55], and the shift between the two
 318 representations $\frac{dN}{d \log D_p}$ and $\frac{dN}{dD_p}$ is always verified to be < 0.1 nm and thus considered as
 319 negligible.

320 CRDS (in-situ) measures the soot volume fraction f_v without giving access to any
 321 information on the PSDF that is hidden in the integral:

$$f_v = \frac{\pi}{6} \int_0^{\infty} D_p^3 \frac{dN}{d \log D_p} d \log D_p \quad \text{Eq. 6}$$

322 On the other hand, SMPS (online) accesses the electrical mobility size distribution
323 $\left(\frac{dN}{d \log D_p}\right)_{\text{SMPS}}$, but cannot provide a reliable measurement of the in-situ total particle number
324 density that is biased by the sampling:

$$\frac{dN}{d \log D_p} = K(D_p) \left(\frac{dN}{d \log D_p}\right)_{\text{SMPS}} \quad \text{Eq. 7}$$

325 Here, the function $K(D_p)$ folds in all sampling-related effects that include the probe and
326 dilution effects during sampling and the particle losses during transport in the probe, in the
327 sampling line and in the SMPS due to diffusion, and depends on a number of factors including
328 D_p .

329 In this work, the same probe and dilution flow were used in all experiments. The
330 uncertainty due to the HAB-dependent temperature on the probed flame volume is small and
331 therefore included in the calculation of the total uncertainty of the particle number density. In
332 order to avoid post-sampling coagulation, preliminary SMPS scans were performed at each
333 HAB by decreasing the differential pressure (thus increasing the dilution ratio) until the particle
334 number density was sufficiently low that no shift of the PSDF to higher D_p could be observed
335 in the time required for the data acquisition. All the PSDFs discussed in this work have been
336 acquired with a dilution ratio equal or higher than this limit.

337 The quantitative estimation of the particle losses due to diffusion during transport is
338 difficult and well beyond the scope of this paper. In this work, a rough estimation was
339 performed by following the theoretical approach proposed by Kulkarni et al. [65] to calculate
340 the transport efficiency function $\eta_{\text{tube,diff}}$ against D_p . The calculated $\eta_{\text{tube,diff}}$ has the highest slope
341 between 2-3 nm, and is roughly twice as large at 5 nm than 2 nm. While experimental
342 estimations of the particle losses for $D_p < 10$ nm exist in the literature [66,67], they are typically
343 determined for very specific experimental conditions or subject to large uncertainty, and thus

344 often regarded as tricky to generalize. For this reason, and to avoid introducing further
 345 uncertainty in the interpretation of the measurements, we decided to discuss the uncorrected
 346 SMPS output, thus de facto neglecting the effect of the particle losses due to diffusion that will
 347 be instead the object of a future dedicated investigation.

348 Under these assumptions, $K(D_p) \approx K$ can effectively be treated as a calibration factor
 349 for the given experimental conditions. In conclusion, the relationship between f_v from *in-situ*
 350 extinction (CRDS) and $\left(\frac{dN}{d \log D_p}\right)_{SMPS}$ from online electrical mobility (SMPS) can be
 351 approximated as:

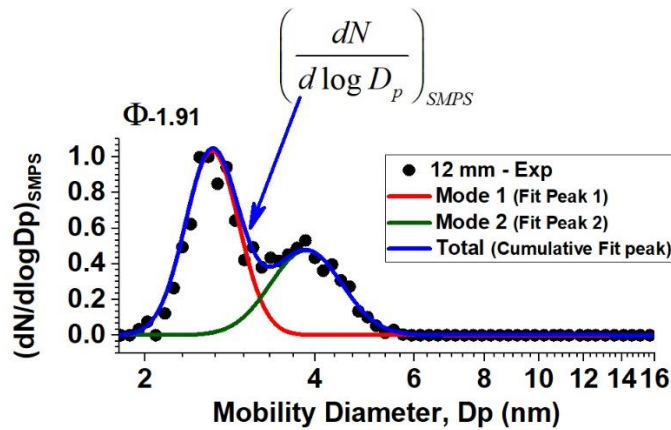
$$f_v = \frac{\pi}{6} K \int_0^{\infty} D_p^3 \left(\frac{dN}{d \log D_p}\right)_{SMPS} d \log D_p \quad Eq. 8$$

352

353 3.2. Application of the method

354 A practical example of the fitting procedure applied to the PSDF measured in the sooting
 355 flame Φ -1.91 at 12 mm HAB is shown in Fig. 2.

356



357

358 Fig. 2: Result of the fitting procedure by using two lognormal functions at the onset of the bimodality
 359 of size distribution at 12 mm HAB in sooting flame Φ -1.91.

360

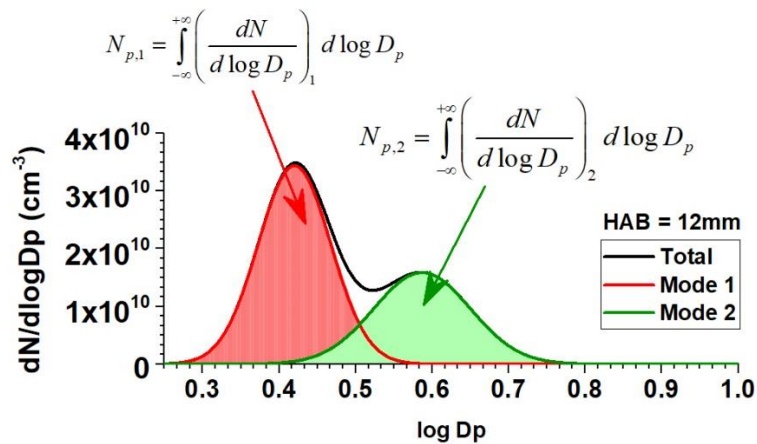
361 As explained above, the method of determination of the soot number density N_p relies
362 on finding the empirical factor K that enables the calibration of the normalized PSDFs reported
363 in SM1 (Fig. S6) obtained by SMPS into absolute number density, with f_v being known from
364 CRDS experiments. This calibration factor K is defined in Eq 7 and independently calculated
365 at each sampled HAB. For instance, at 12 mm HAB in the flame Φ -1.91:

$$K_{12\text{mm}} = \frac{f_v}{\frac{\pi}{6} \int_0^\infty D_p^3 \left(\frac{dN}{d \log D_p} \right)_{\text{SMPS}} d \log D_p} = \frac{1.24 \times 10^{-10}}{3.74 \times 10^{-21}} \approx 3.32 \times 10^{10} \quad \text{Eq. 9}$$

366 The integration of the PSDF allows deducing, according to Eq. 4, the total number
367 density of soot particles that in the example at 12 mm HAB: $N_p = 6.59 \times 10^9 \text{ cm}^{-3}$. This protocol
368 can be extended to the determination of the number density of soot particles in the different
369 modes (mode 1 and mode 2) of the PSDF, as graphically shown in Fig. 3 ($N_{p,1} = 4.09 \times 10^9 \text{ cm}^{-3}$
370 3 , in red and $N_{p,2} = 2.50 \times 10^9 \text{ cm}^{-3}$, in green).

371 This procedure has been applied to all the investigated flames to obtain the absolute soot
372 numbers density profiles presented and discussed in the following sections.

373



375 Fig. 3: Determination of number density of mode 1 and 2 of soot particles at 12 mm HAB in the flame
376 Φ -1.91.

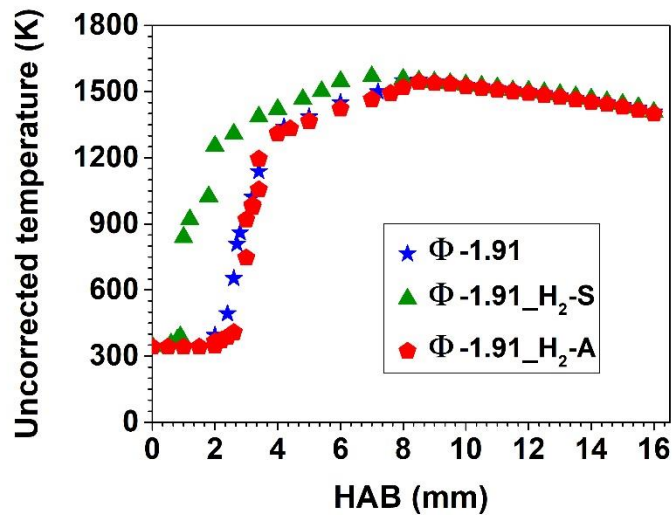
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378

379 **4. Results and discussion**

380 **4.1. Effect of H₂ on the flame temperature profiles**

381 Fig. 4 displays the experimental temperature profiles obtained with a coated Pt/Rh(6%)-
382 Pt/Rh(30%) thermocouple for the three studied flames (Φ -1.91, Φ -1.91_H₂-S, and Φ -1.91_H₂-
383 A). The reported temperatures were not corrected from the radiative heat loss. As it can be seen,
384 the H₂ substitution (Φ -1.91_H₂-S) shifts the temperature profile toward the burner surface due
385 to the laminar flame velocity increase (see Table 1), while the addition procedure (Φ -1.91_H₂-
386 A) does not cause any shift. Indeed, the laminar flame velocity of flame Φ -1.91_H₂-S has been
387 determined to be around 9.9 m/s which was higher than that calculated in flame Φ -1.91 around
388 9.2 m/s. By contrast, the laminar flame velocity of flame Φ -1.91_H₂-A around 9.1 m/s is close
389 to that of reference flame Φ -1.91. In both approaches (addition or substitution), as expected by
390 such a small introduction of H₂ (1.8%), all studied flames exhibit similar temperature peak,
391 confirming the negligible influence of the additional H₂. Hence, the temperature measured in
392 the post flame region where soot particles are formed and growing are very close in the three
393 studied flames. The adiabatic temperature calculated using GASEQ [39] confirms the very
394 limited impact of H₂ on the flame temperature profiles as shown in Table 1. The absence of
395 modification in the three measured temperature profiles (except the slight shift towards the
396 burner of the whole profile in the case of H₂ substitution) therefore allows attributing the change
397 of the mole fraction of PAHs and soot volume fraction to the effect of H₂ and not to the
398 temperature.

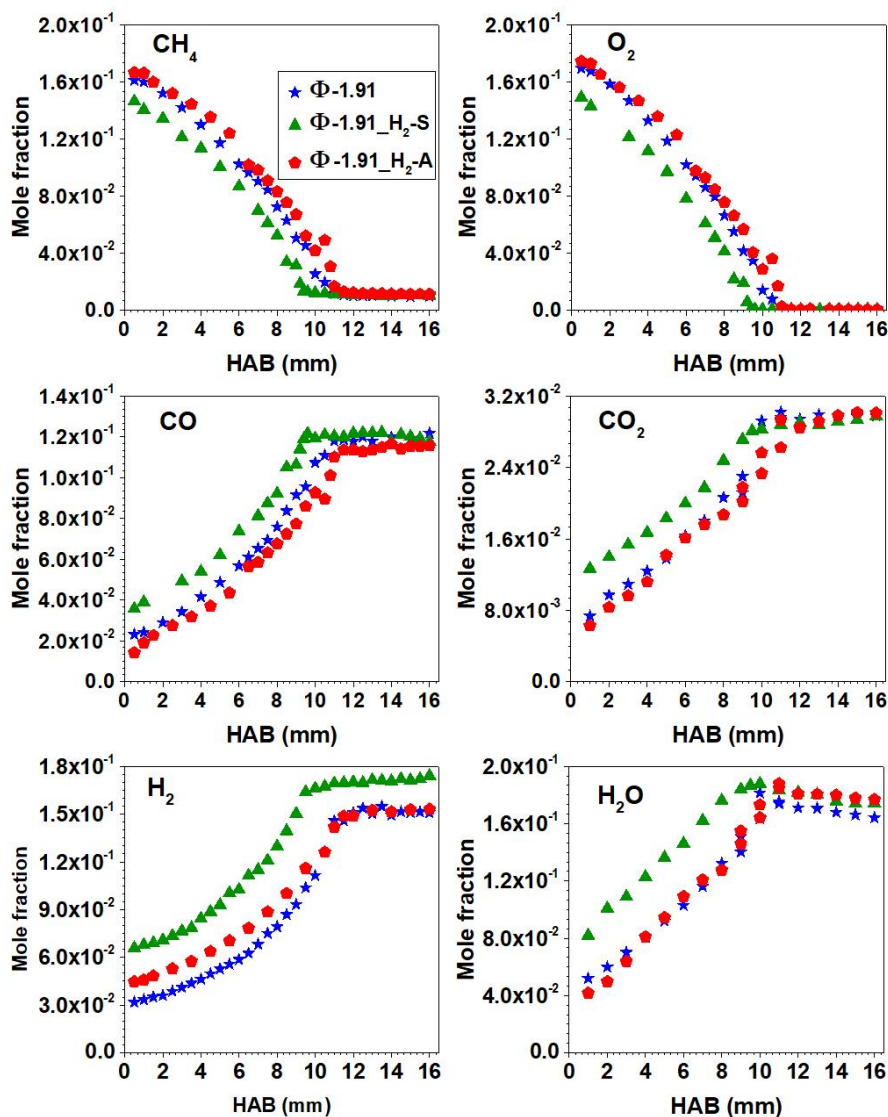


399 Fig. 4: Impact of H₂ on the uncorrected flame temperature profiles. Φ-1.91: CH₄ flame; Φ-1.91_H₂-S:
 400 CH₄ substituted-H₂ flame; Φ-1.91_H₂-A: CH₄ added-H₂ flame (see Table 1 for the flame conditions).

401

402 4.2. Effect of H₂ on major species (reactants and combustion products)

403 Fig. 5 reports the mole fraction profiles of the main species including reactants (fuel,
 404 O₂) and final products (CO, CO₂, H₂, H₂O) for the three studied flames. As observed for the
 405 temperature profiles presented above, the H₂ substitution (Φ-1.91_H₂-S) systematically shifts
 406 the profiles of the major species around 2 mm closer to the burner surface while the H₂ addition
 407 (Φ-1.91_H₂-A) does not significantly modify the flame position. The explanation for this effect
 408 is the same as the explanation for the temperature profiles discussed in Section 4.1. Briefly, this
 409 shift can be explained by the laminar flame velocity increase in the case of H₂ substitution
 410 (Φ-1.91_H₂-S). By contrast, in the case of H₂ addition (Φ-1.91_H₂-A), no significant
 411 modification of the flame velocity is calculated and therefore no significant influence on the
 412 flame position. It is to be noted that the higher mole fractions of H₂ observed at HABs from
 413 0 mm to 11 mm in the latter flame compared to the reference flame are simply due to the added
 414 H₂ fraction in the initial gas mixture. The impact of H₂ on the evolution of the mole fraction
 415 profiles of the reactants and final products obtained in the three flames is similar as the one
 416 observed in the three nucleation flames reported in our recent work [32].

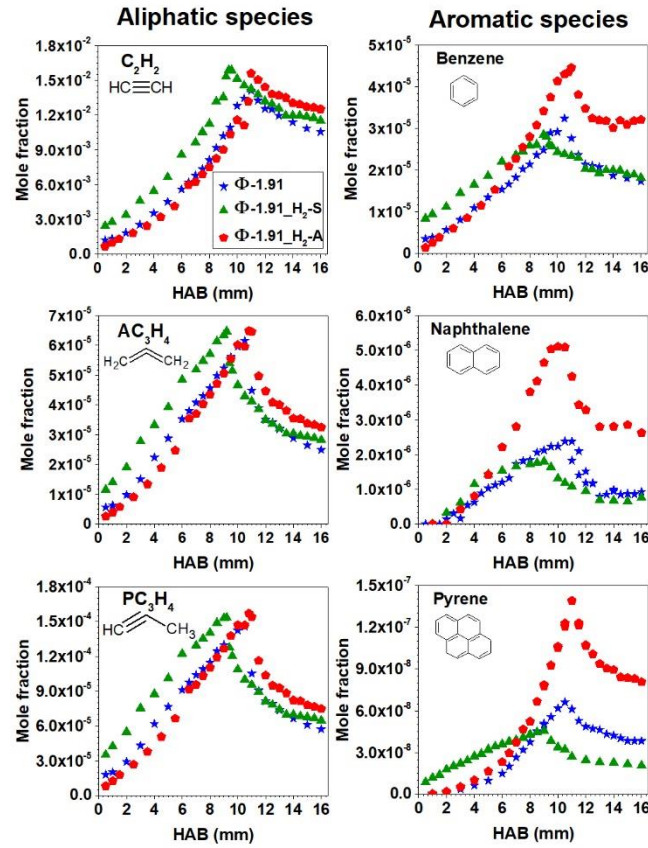


417
 418 Fig. 5: Mole fraction profiles of reactants (fuel, O₂) and major products (CO, CO₂, H₂, H₂O) obtained
 419 in the three studied flames.
 420

421 4.3. Effect of H₂ on soot precursors

422 Fig. 6 shows the mole fraction profiles of some aliphatic and aromatic species in the
 423 three flames. We present here the mole fraction profiles of acetylene (C₂H₂), allene (AC₃H₄)
 424 and propyne (PC₃H₄) which are considered as important precursors of the first aromatic ring,
 425 PAHs and soot [68–71]. The mole fraction profiles of other aliphatic species analyzed in this
 426 work are available in SM1 (Fig. S2). Fig. 6 also displays the measured mole fraction profiles

427 of three aromatic compounds (benzene C₆H₆, naphthalene C₁₀H₈ and pyrene C₁₆H₁₀) which are
 428 considered as crucial soot precursors [32,72–74].



429
 430 Fig. 6: Mole fraction profiles of aliphatic species (acetylene, allene, propyne) and aromatic species
 431 (benzene, naphthalene and pyrene) obtained in the three studied flames.

432
 433 The H₂ substitution shifts the mole fraction profiles of all gaseous species around 2 mm
 434 closer to the burner surface because of the increase of the laminar flame velocity as presented
 435 in Table 1, consistently with the consumption behavior, while H₂ addition does not induce any
 436 significant effect on the position of the mole fraction profiles of the detected species in the gas
 437 phase. Both H₂ substitution and addition show no significant effect on the peak values of the
 438 mole fraction of the aliphatic species. However, the presence of H₂ in the sooting flame Φ-1.91
 439 strongly impacts the formation of aromatic species (Fig. 6). The H₂ substitution (Φ-1.91_H₂-S)
 440 exhibits an inhibitory effect (12-31%) on benzene, naphthalene, and pyrene formation whereas

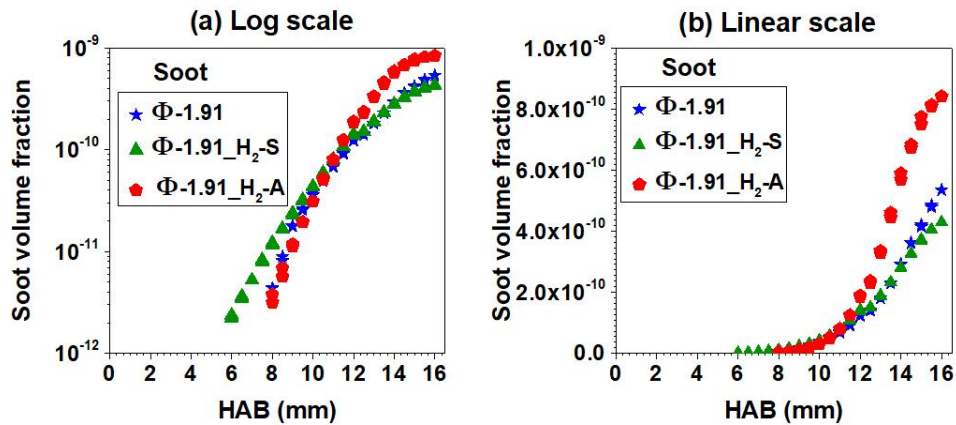
441 the H₂ addition (Φ -1.91_H₂-A) clearly promotes their formation (30-53%). Such antagonistic
442 effect was also observed for the nucleation flames in our recent work [32]. In this work we have
443 also shown that the impact of H₂ can be specifically attributed to a chemical effect rather than
444 dilution. Indeed, substituting the equivalent of 1.8% of N₂ by He did not affect the mole fraction
445 profiles of benzene and aliphatic species in any flames as shown in SM1 (Fig. S3).

446 A detailed explanation of the chemical effect of H₂ on aromatic species was given in
447 our previous work [32]. The same mechanism could be considered for the present flames, as
448 summarized in Fig. S4. Under flame conditions, H₂ can be converted to H-atoms through
449 several reactions, such as $\text{H}_2 + \text{OH} \rightarrow \text{H} + \text{H}_2\text{O}$, $\text{H}_2 + \text{O} \rightarrow \text{H} + \text{OH}$, and $\text{H}_2 + \text{M} \rightarrow \text{H} + \text{H} + \text{M}$. The H₂
450 effect is then the result of different competitive processes that share the resulted H-atoms as a
451 reactant. As showed in Fig. S4 (left panel), the high temperature branching reaction $\text{H} + \text{O}_2 =$
452 $\text{O} + \text{OH}$ (path A) competes with the benzene/PAH accumulation process (path B), the PAH
453 growth processes (path C), and the soot particle growth processes (paths D and E) that are
454 significant in the fuel richer flames. As showed in the right panel of Fig. S4 in the case of
455 substitution, the path A is reinforced by the presence of H₂ which is proved by the observed
456 increase of the laminar flame speed (Table 1). In these conditions, the H-atoms are thus largely
457 converted to OH and O, resulting in the acceleration of the oxidation processes of aromatic
458 species and in the decrease of the H-atoms available for the PAH growth through the HACA
459 mechanism. These points explain the decrease of the mole fractions of the aromatic species
460 under the H₂ substitution conditions.

461 In the case of H₂ addition, the reaction $\text{H} + \text{O}_2 = \text{O} + \text{OH}$ is not favored. This is
462 confirmed by the flame front position and by the calculated laminar flame speed, which
463 highlighted similar values for the flame with added H₂ (Φ -1.91_H₂-A) and the reference flame
464 (Φ -1.91) as reported in Table 1. Thus, H-atoms from H₂ addition would primarily participate
465 to the benzene/PAHs formation by termination reactions, promoting aromatic formation.

466 4.4. Effect of H₂ on soot formation

467 The measured soot volume fraction profiles determined for the three studied flames are
468 reported in Fig. 7. The H₂ substitution shifts the soot volume fraction f_v profile around 2 mm
469 closer to the burner surface, while H₂ addition does not induce this effect (Fig. 7a). The effect
470 of H₂ on the position of the f_v profile is consistent with that of the gaseous soot precursors as
471 reported in Fig. 6. The H₂ substitution decreases while H₂ addition increases the maximum f_v .
472 Hence, the impact of H₂ on the soot quantities generated in flame Φ -1.91 may be directly related
473 to the formed PAHs mole fractions as discussed above.
474



475
476 Fig.7: Soot volume fraction profiles measured in the three studied flames by LII /CRDS. (a) log scale
477 and (b) linear scale.
478

479 4.4.1. Hypothesis about a PAH concentration threshold for soot nucleation

480 In flame Φ -1.91_H₂-S, we carefully determined by LII the HAB corresponding to the
481 beginning of the soot formation according to the sensitivity of our optical setup (first
482 measurable LII signals). Hence this point has been established at 6 mm HAB for this flame and
483 the corresponding soot volume fraction at this HAB has been determined to be around 2 ppt,
484 i.e. a value similar to that previously measured at the soot starting point of the nucleation flames

485 [32]. The corresponding mole fractions of benzene, naphthalene and pyrene at this HAB were
486 determined around 22 ppm, 1.5 ppm and 36 ppb, respectively, which are very close to the values
487 measured at the onset of the soot nucleation point of the previously studied nucleation flames
488 [32]. This observation therefore supports the hypothesis already suggested in [32] of a PAH
489 concentration thresholds, potentially independent of the flame operating conditions and nature
490 of the fuel, triggering the soot nucleation process. Unfortunately, the determination of this onset
491 point in the other two flames was affected by higher uncertainty. Regarding our data, and
492 notably the signal-to-noise ratio (SNR) of the LII signal measured at 8 mm, corresponding to
493 the lowest studied HAB by LII in the Φ -1.91 and Φ -1.91_H₂-A flames (Fig S.5b and c), it is
494 clear that the SNR appears much better than that observed at 6 mm in flame Φ -1.91_H₂-S.
495 Hence, it is likely that the onset of the soot nucleation point for these two flames is located a
496 little upstream 8 mm. However, the soot volume fractions determined at 8 mm in the flame
497 Φ -1.91 ($f_v=4.4$ ppt) and flame Φ -1.91_H₂-A ($f_v=3.2$ ppt) are still very close to that at the onset
498 of the soot nucleation point in flame Φ -1.91_H₂-S ($f_v=2$ ppt). Moreover, it is noteworthy that
499 the mole fractions reported in Table 2 of benzene, naphthalene and pyrene measured at the onset
500 of the soot nucleation points in the three flames (Φ -1.91 flame, Φ -1.91_H₂-A, Φ -1.91_H₂-A)
501 are similar and also very close those of previously investigated nucleation flames [32] (see also
502 Table 2). These data support therefore the idea of a PAH concentration threshold required to
503 initiate the soot nucleation process. However, it is clear that more experimental work, especially
504 involving other fuels, is required to confirm this hypothesis.

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| Flame | Mole fractions (soot starting point) | | |
|---|--------------------------------------|-------------------|--------------|
| | Benzene (ppm) | Naphthalene (ppm) | Pyrene (ppb) |
| Φ -1.91 | 21 | 1.8 | 38 |
| Φ -1.91_H ₂ -S | 22 | 1.5 | 36 |
| Φ -1.91_H ₂ -A | 28 | 3.8 | 52 |
| Φ -1.82 / Φ -1.82_H ₂ -S / Φ -1.82_H ₂ -A [32] | 16 | 1.3 | 22 |

510

511 Table 2: Mole fractions of aromatic compounds determined at the onset of the soot nucleation in the
512 three rich flames Φ -1.91 and previously studied nucleation flames Φ -1.82 [32].

513

514 4.4.2. Effect of H₂ on the particle size distribution function

515 In this section, the impact of H₂ on the soot particle diameter and number density and
516 more specifically on its influence on the growth mechanism of soot formation is discussed in
517 detail. Fig. 8 presents the PSDFs measured from SMPS, LII and CRDS experiments against
518 HABs in the three studied flames. As it can be seen in this figure, the first measurable PSDFs
519 by SMPS in these flames appears at slightly higher HABs than the detection of the first LII
520 signals reported in Fig. 7. In the absence of a deeper comparison between the two techniques,
521 it is difficult to conclude about the origin of this small shift, which might be due to several
522 reasons as a lower detection limit of the LII setup or the flame perturbation induced by the
523 probe sampling required for the SMPS measurements. However, this small discrepancy
524 suggests that our microprobe only slightly perturbs the flame front, which validates the
525 complementary use of these techniques implemented here to characterize the soot formation.

526

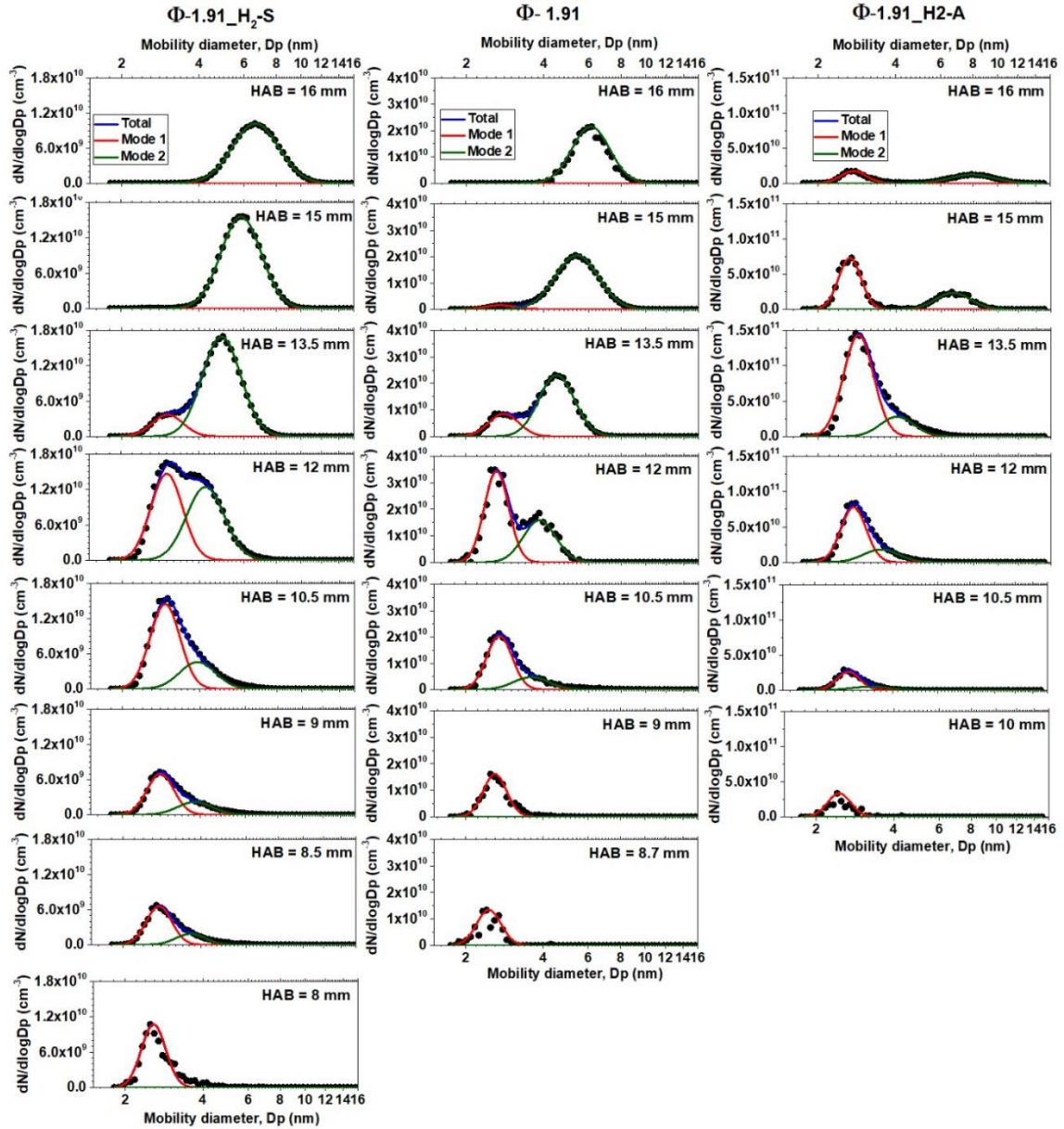
527 Concerning the Φ -1.91 flame, as already observed in the literature [75–77], we notice
528 at the lowest HABs the appearance of a single mode characterized by a fixed diameter all along
529 the flame height, followed by the formation of a second mode higher in the flame, highlighting

530 the growing particles. The first PSDF measured at 8 mm HAB, that characterizes the nascent
531 soot particles generated in the nucleation process, features a monomodal lognormal distribution
532 centered around 2.5 nm (mode 1). The monomodal distribution exists only up to 10.5 mm HAB.
533 Above 10.5 mm HAB, a bimodal distribution appears. While mode 1 does not shift to higher
534 D_p as the HAB increases, mode 2, newly appeared at 10.5 mm HAB and initially centered at
535 3.2 nm, shifts to higher D_p as HAB increases. The existence and shift of mode 2 point to the
536 competition between nucleation, coagulation and surface reactions as already well established
537 in the literature [58,77–79]. At 12 mm HAB, mode 2 appears more clearly and mode 1 reaches
538 its maximum intensity. Above 12 mm HAB, mode 1 begins to decrease and disappears
539 completely at 15 mm HAB, suggesting that the nucleation process is no longer active above
540 this HAB probably because of the diminution of the concentration of aromatic soot precursors
541 in the flame. Fig. 9 presents the evolution of the median diameter of mode 1 and 2 against HAB
542 for the three studied flames. We observe that the median diameter of mode 1 is constant against
543 HAB and that the median diameter of mode 2 increases gradually. This dynamic suggests that
544 the soot growth process in flame Φ -1.91 are dominated by the HACA mechanism and by PAHs
545 condensation on the soot surface rather than coagulation/coalescence processes.

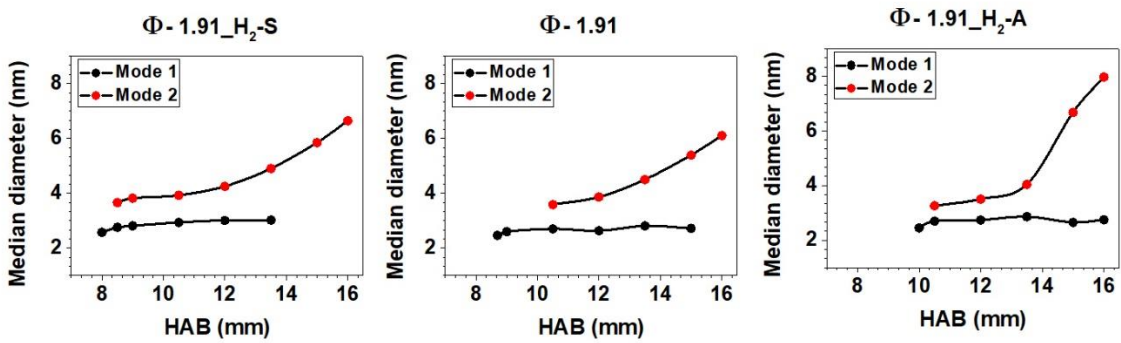
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547 Concerning the influence of H₂ (Φ 1.91_H₂-S and Φ 1.91_H₂-A flames), Figs. 8 and 9
548 show that both H₂ substitution and addition do not influence the PSDF (median diameter and
549 geometric standard deviation) of mode 1. This result indicates that the mechanism of nascent
550 soot formation from gaseous precursors is probably similar in the three studied flames, which
551 will be further discussed in the next section. The end of the nucleation process observed in the
552 Φ -1.91_H₂-S flame at 15 mm HAB is similar to the reference flame Φ -1.91. By contrast, it is
553 noteworthy that the formation of nascent soot particles in flame Φ -1.91_H₂-A is promoted
554 along the whole flame height.

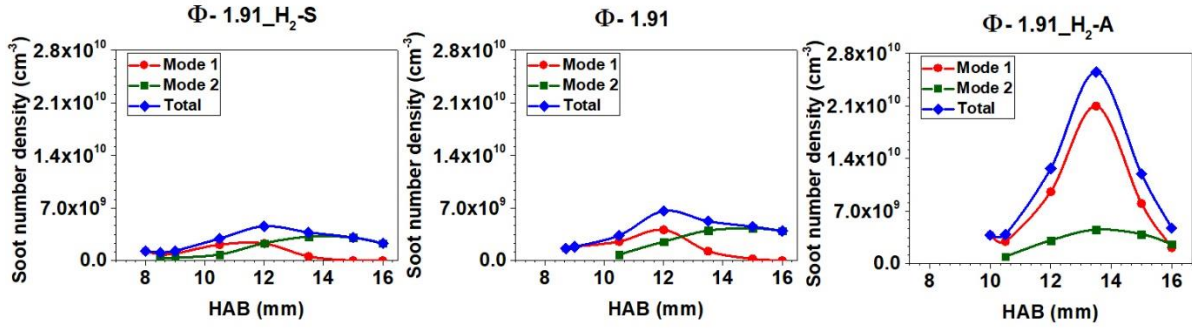
555 Fig. 10 shows the evolution of the soot number density of mode 1, mode 2 and the total
556 soot number density in the three studied flames. H₂ substitution slightly decreases the maximum
557 soot number density of mode 1 while H₂ addition strongly increases this value. This decrease
558 or increase of mode 1 with the H₂ substitution or addition could be a result of a decrease or an
559 increase in the formation of aromatic species, respectively, as shown in Fig. 6. Above 15 mm
560 in the two flames Φ -1.91 and Φ -1.91_H₂-S, the mole fraction of aromatic species is low (Fig.
561 6). Hence, aromatic species can not initiate anymore the soot nucleation process. By contrast,
562 in the Φ -1.91_H₂-A, the H₂ addition strongly increases the formation of aromatic species. In
563 this case, the mole fraction of these species is always above the aromatic concentration
564 threshold associated to the formation of the very first soot particles [32] and this, even for the
565 higher HAB in this flame. In this case, the nucleation process is always active along the flame
566 height in flame Φ -1.91_H₂-A. These data therefore again point out to the need of a minimum
567 concentration of PAHs required for the activation of the soot nucleation process



568 Fig. 8: Particles size distribution functions measured by SMPS, LII and CRDS obtained in the three
 569 studied flames.



570 Fig. 9: Median diameter of mode 1 and mode 2 against HAB obtained by fitting the PSDFs in the three
 571 studied flames.



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Fig. 10: Evolution of soot number density against HAB in the three studied flames.

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Regarding the soot growth process, based on the evolution of the measured PSDFs (Fig. 8), we can deduce that the dynamic of these processes in the flame Φ -1.91_H₂-S is quite similar to that in flame Φ -1.91. Indeed, mode 2 in this flame appears gradually as shown in Fig. 9, and similarly the median diameter of mode 2 increases gradually at higher HAB. This suggests a soot growth process mainly driven by surface growth processes as the HACA mechanism and PAHs condensation on soot surface in these two flames. However, it is noteworthy that the H₂ substitution shifts the onset of the soot growth process to lower HAB than that in flame Φ -1.91. Indeed, according to Fig. 6, the H₂ substitution also shifts to lower HAB the mole fraction profile of soot precursors as C₂H₂ and aromatic species. The median diameter of mode 2 at 16 mm HAB in flame Φ -1.91_H₂-S is therefore slightly higher than in flame Φ -1.91 because the residence time of soot particles for soot growth process in the flame Φ -1.91_H₂-S is slightly longer than in the flame Φ -1.91. Finally, the H₂ substitution decreases the soot number density of mode 2 and total soot number density because of the diminution of the initial quantity of nascent soot particles formed in this flame.

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In flame Φ -1.91_H₂-A, mode 2 initially appears very close to mode 1 at 10.5 mm HAB, characterized by a median diameter evolving from 3.3 to 4.1 nm between 10.5 and 13.5 mm HAB, similar to the reference flame. However, by contrast with the reference flame Φ -1.91, in the Φ -1.91_H₂-A, mode 2 against HAB shows a substantial change of slope around 13.5 mm

593 HAB as shown in Fig. 9. The evolution of this mode, very different from that observed in the
594 reference flame Φ -1.91, indicates the predominance of additional growth processes to those
595 observed in the reference flame Φ -1.91, probably coagulation and/or coalescence. The sudden
596 appearance of this mode 2 with median diameter 6.7 nm at 15 mm is indeed consistent with a
597 stronger efficiency of the coagulation/coalescence processes of the particles of the mode 1 with
598 a median diameter of 2.6 nm.

599 If this hypothesis is correct, the predominance of the coagulation/coalescence growth
600 processes might be correlated with the larger number of soot particles formed in the flame
601 Φ -1.91_H₂-A due to the addition of H₂ and therefore to the greater probability of particle
602 collisions under these conditions. As shown in Fig. 10, H₂ addition strongly increases the
603 number of soot particles of mode 1 compared to reference flame Φ -1.91, clearly highlighting
604 the major role of H₂ in the nucleation process. The increase of nascent soot particles number
605 density stops at 13.5 mm HAB and a drastic decrease of nascent soot particles is then observed
606 between 13.5 and 15 mm HAB, directly correlated to the appearance of the isolated mode 2. It
607 is interesting to note that this specific evolution only appears in this flame in which the quantity
608 of nascent soot particles is up to 5 times higher than that in the reference flame Φ -1.91. The
609 ensemble of the experimental data seems to suggest the existence of a threshold value for the
610 particle concentrations above which the coagulation/coalescence processes would become
611 dominant due to a greater probability of collision of soot particles. A complete understanding
612 of this phenomena would require detailed modelling that was beyond the scope of this work
613 and will be the subject of further investigations.

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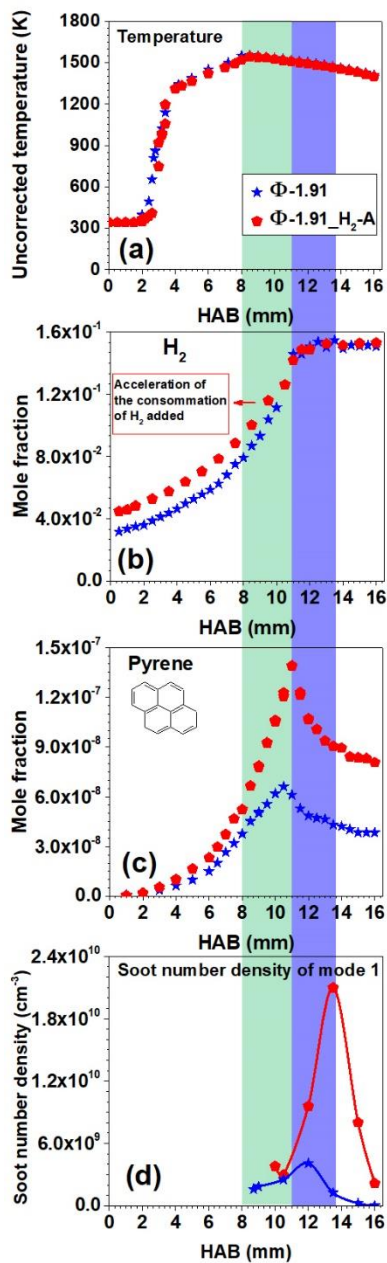
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618 4.4.3. Effect of H₂ on nascent soot particles

619 As observed in Section 4.4.2, the H₂ addition induces a persistence of the soot nucleation
620 process all along the flame height characterized by the presence of the mode 1 in substantial
621 number density. To further explore the effect of H₂ addition on the nucleation process in sooting
622 flame Φ -1.91, Fig.11 recaps the profiles of temperature, H₂, pyrene and soot number density of
623 mode 1 in the two flames Φ -1.91, Φ -1.91_H₂-A.

624 As already stated, H₂ addition does not impact the temperature profile reported in Fig.
625 11a. Therefore, the observed modifications in the formation of aromatic species and soot
626 reported in Fig.11c,d is rather related to the chemical effect due to the addition of H₂. We
627 observe in Fig. 11b that the mole fraction of H₂ near the burner surface of flame Φ -1.91_H₂-A
628 is higher than in the reference flame Φ -1.91 and tends to approach the mole fraction profile of
629 H₂ of the reference flame from 8 mm up to 10.5 mm HAB (green area in the figure). The mole
630 fraction of pyrene increases strongly in this zone due to the H₂ addition (Fig. 11c). As discussed
631 earlier, the consumption of H atoms from the H₂ addition mainly serves to termination reactions
632 involving aromatic radicals and yields stable aromatic compounds. Above 10.5 mm, the mole
633 fraction of H₂ measured in the two flames Φ -1.91, Φ -1.91_H₂-A is similar. Therefore, the soot
634 nucleation process after the pyrene peak is mainly impacted by a higher concentration of PAHs
635 due to the H₂ addition, and resulting in the formation of a large number of nascent soot particles
636 after the pyrene peak in flame Φ -1.91_H₂-A (10.5 – 13.5 mm, violet zone in the figure). The
637 large number density of nascent soot particles at 13.5 mm HAB increases the
638 coagulation/coalescence rate and results in the drastic reduction of the soot particles number
639 density above this zone and the concomitant appearance of mode 2 centered around 6.7 nm at
640 15 mm HAB (see Fig. 8).



641

642 Fig. 11: Profiles of temperature, and mole fraction of H₂, pyrene and soot number density of mode 1 in

643 the two flames Φ-1.91 (blue), Φ-1.91_H₂-A (red). The green zone defines the accumulation of

644 aromatic species; the violet zone defines the consumption of aromatic species for nascent soot

645 formation. The line in Fig. 11d has been added to the plot to guide the eye.

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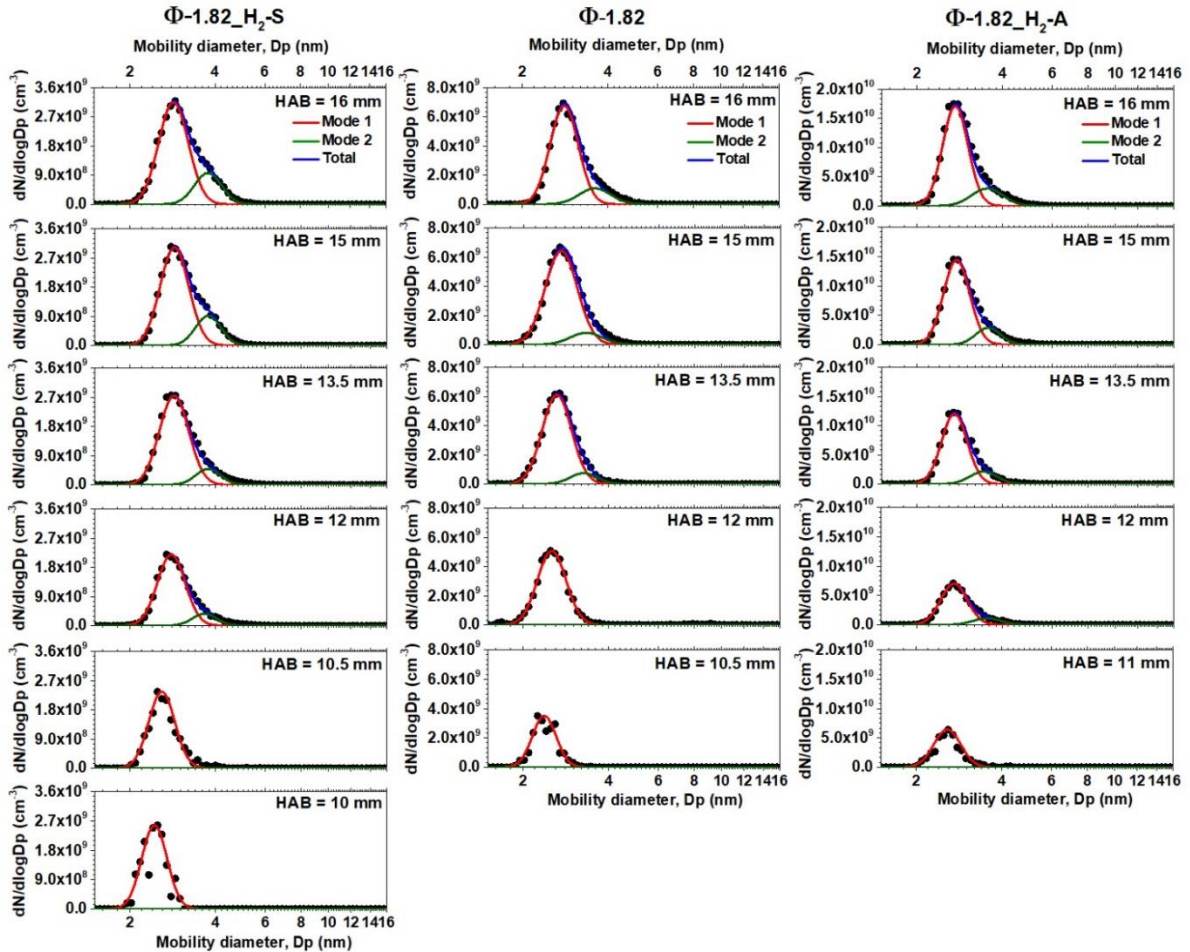
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648 This statement can be further corroborated by the analysis of previous experiments we
649 carried out in slightly a sooting methane flame (Φ -1.82) [32] generating much less PAHs and
650 soot particles than the Φ -1.91 flames. In this work, we also slightly perturbed the reference
651 Φ -1.82 flame by H_2 addition or substitution according to the same protocol as used for the
652 Φ -1.91. The PSDFs of the soot particles in these flames (not reported in [32]) was newly
653 measured in the present work and reported in Fig. 12. The determination of the absolute soot
654 number density N_p has been carried out according to the method described section 3.1, using
655 the normalized PSDFs obtained by SMPS reported in SM1 (Fig. S8).

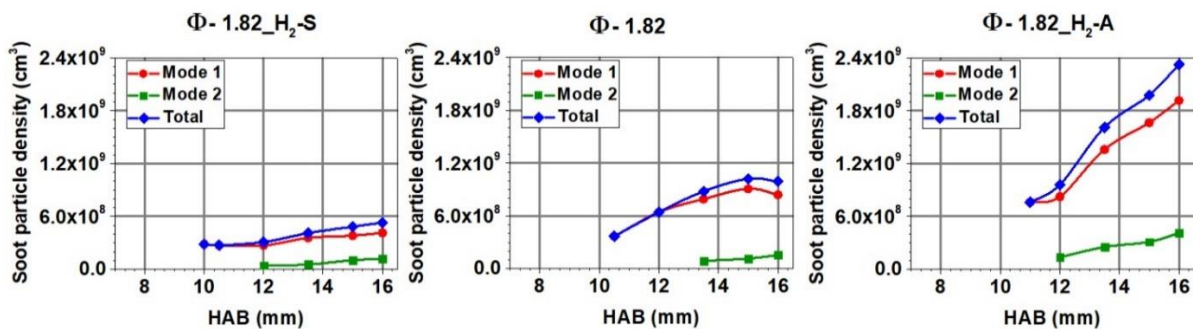
656 The Φ -1.82 reference flame has been defined as a nucleation flame, i.e. a flame
657 generating soot particles which do not undergo or very limited growth processes all along the
658 flame height. Hence, the soot PSDFs for this flame are characterized by almost one mode. As
659 can be seen in SM1 (Fig. S9), this mode highlights a quasi-constant median diameter around
660 2.6 nm all along the flame height, similar to the mode 1 characterizing the nascent soot particles
661 generated in the Φ -1.91 flames. A much weaker second mode however appears at 13.5 mm
662 HAB, indicating that soot growth processes are still somewhat activated in the nucleation flame
663 Φ -1.82, but actually well balanced by oxidation along a large part of the flame, precluding the
664 growth of the soot particles excepted at the highest HABs [38].

665 According to Fig. 12, the introduction of H_2 , either by addition or substitution, in these
666 nucleation flames, does not impact the PSDF of the generated soot particles. By contrast, the
667 introduction of H_2 in the nucleation flame Φ -1.82 strongly impacts the formation of aromatic
668 species and soot volume fraction [32] as well as the soot number density as reported in Fig. 13.
669 Similarly to the observations made for the Φ -1.91 flame, the H_2 substitution in the nucleation
670 flame Φ -1.82 decreases the nascent soot particles number density while the H_2 addition strongly
671 increases the nascent soot particles number density. However, the H_2 addition in the nucleation
672 flame does not seem to modify the soot growth dynamic by enhancing the

673 coagulation/coalescence processes as observed in the richer flame Φ -1.91_H₂-A, probably
 674 because of the much lower number density of soot particles (around 10 times less) generated in
 675 the flame Φ -1.82_H₂-A in comparison with the Φ -1.91-A, therefore limiting the probability of
 676 collision of soot particles.



677 Fig. 12. Particles size distribution functions measured by SMPS obtained in the three methane
 678 nucleation flames.



680 Fig. 13. Evolution of soot number density in the three methane nucleation flames.

681 **5. Conclusion**

682 This work reports new experimental data obtained in three atmospheric sooting
683 premixed methane flames with and without added/substituted H₂ (~10% molar comparing to
684 CH₄ fuel, at $\Phi_C=1.91$). An original analytical methodology has been developed relying on the
685 coupling of the data obtained by SMPS and LII/CRDS measurements to determine the soot
686 number density. This method does not require accurate knowledge of the dilution in the
687 sampling line, which is a strong limitation for quantitative SMSP measurements of particle
688 number density.

689 Our results clearly show the influence of H₂ as a fuel additive to the formation of soot
690 precursors, soot nucleation and soot growth. Similarly to previous observations on nucleation
691 flames [32], the results obtained in the presented fuel-richer flames notably show that the
692 introduction of H₂ strongly influences the concentration of aromatic species and soot, either
693 increasing or decreasing, that depends on the operating conditions (H₂ addition or substitution).
694 Finally, the invariance of the concentration of PAHs and the soot volume fraction measured at
695 the beginning of the soot formation in the sooting flames $\Phi=1.91$, similarly to previous
696 experiments carried out in different nucleation flames, again supports the idea that onset of the
697 soot particle might be controlled by specific concentrations thresholds of aromatic precursors
698 already mentioned in [32].

699 Regarding the soot size distribution, we observed that neither H₂ substitution nor H₂
700 addition influence the PSDF and in particular the median diameter of mode 1 featuring the
701 nascent particles either in the rich flames $\Phi=1.91$ or in the nucleation flame $\Phi=1.82$. This result
702 indicates that the mechanism of nascent soot formation from gaseous precursors is probably
703 similar in the three studied flames. The H₂ substitution in the flame does not influence the
704 mechanism of soot growth, either. By contrast, we observe in the case of H₂ addition a
705 substantial modification in the dynamic of the soot growth processes. This modification might

706 be due a better efficiency of the coagulation/coalescence processes because of the strong
707 increase in the number of nascent soot particles. The H₂ addition indeed promotes the
708 accumulation of PAHs in the area preceding the pyrene peak through termination reactions
709 involving H atoms and PAH radicals. The accumulation of aromatic species prior to the pyrene
710 peak provides a large reservoir of nascent soot particles molecular precursors resulting in the
711 increase in the number of these particles after the pyrene peak. This large increase of the number
712 of nascent soot particles in the Φ -1.91_H₂-A flame might therefore favor the
713 coagulation/coalescence processes thus promoting their size increase in the burnt gas zone.
714 From this study, we hypothesized the existence of a soot particle number density threshold
715 above which the coagulation/coalescence processes might become more effective due to a
716 greater probability of collision of soot particles. However, only the use of detailed soot growth
717 models will enable an accurate description of the real dynamic and of the involved equilibria
718 between the different soot growth processes taking place in these flames. This detailed
719 modeling study will certainly be investigated in the near future.

720

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982 **Figure Captions:**

983 Fig.1: Normalized fluence curves at 0.2 J/cm^2 obtained in three studied flames. Φ -1.91: CH_4
984 sooting reference flame; Φ -1.91_H2-S: CH_4 substituted- H_2 flame; Φ -1.91_H2-A: CH_4 added-
985 H_2 flame.

986 Fig. 2: Result of the fitting procedure by using two lognormal functions at the onset of the
987 bimodality of size distribution at 12 mm HAB in sooting flame Φ -1.91.

988 Fig. 3: Determination of number density of mode 1 and 2 of soot particles at 12 mm HAB in
989 the flame Φ -1.91.

990 Fig. 4: Impact of H_2 on the uncorrected flame temperature profiles. Φ -1.91: CH_4 flame; Φ -
991 1.91_H2-S: CH_4 substituted- H_2 flame; Φ -1.91_H2-A: CH_4 added- H_2 flame (see Table 1 for the
992 flame conditions).

993 Fig. 5: Mole fraction profiles of reactants (fuel, O_2) and major products (CO , CO_2 , H_2 , H_2O)
994 obtained in the three studied flames.

995 Fig. 6: Mole fraction profiles of aliphatic species (acetylene, allene, propyne) and aromatic
996 species (benzene, naphthalene and pyrene) obtained in the three studied flames.

997 Fig.7: Soot volume fraction profiles measured in the three studied flames by LII /CRDS. (a)
998 log scale and (b) linear scale.

999 Fig. 8: Particles size distribution functions measured by SMPS, LII and CRDS obtained in the
1000 three studied flames.

1001 Fig. 9: Median diameter of mode 1 and mode 2 against HAB obtained by fitting the PSDFs in
1002 the three studied flames.

1003 Fig. 10: Evolution of soot number density against HAB in the three studied flames.

1004 Fig. 11: Profiles of temperature, and mole fraction of H_2 , pyrene and soot number density of
1005 mode 1 in the two flames Φ -1.91 (blue), Φ -1.91_H2-A (red). The green zone defines the

1006 accumulation of aromatic species; the violet zone defines the consumption of aromatic species
1007 for nascent soot formation. The line in Fig. 11d has been added to the plot to guide the eye.

1008 Fig. 12. Particles size distribution function measured by SMPS obtained in the three methane
1009 nucleation flames.

1010 Fig. 13. Evolution of soot number density in the three methane nucleation flames.

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