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OPTICAL DETERMINATION OF INCIPIENT SOOT PARTICLE CONCENTRATIONS IN ETHENE LAMINAR DIFFUSION FLAMES

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ABSTRACT

Recent studies in premixed flames have shown the existence of "transparent particles." These particles, 2 nm in size and in high number densities are considered to be a phase transitional between the gas phase PAH species and particulate soot. In the present study, various optical diagnostics were evaluated for measuring the concentration of these particles *in situ.* Through such evaluations, a technique using extinction at two wavelengths was found to be ideal. While employing such a technique, the volume fractions of these particles in an ethene laminar diffusion flame were measured. Low in the flame, these particles were found to be concentrated in the fuel rich core, while at higher locations, they could be found with appreciable volume fractions even in the soot laden regions. Having given due consideration for the errors due to uncertainties in the optical constants, we report the existence of these particles in an ethene flame with volume fractions comparable to those of soot. Also, similar measurements performed in a low sooting ethene+methanol flame show the concentration of these particles to be of the same order of magnitude as in a pure ethene flame.

Nomenclature

f_{vs}	soot volume fraction (ppm)
f_{vp}	transparent particle volume fraction (ppm)
$\alpha,\beta,\gamma,\delta$	constants determined by the optical properties of soot and of 'transparent particles, (/μm)
Q_{hv}	Scattering cross-section determined by having incident laser at vertical polarization and the signal collection at horizontal polarization, (cm^{-1} Sr^{-1})
Q_{vv}	Scattering cross-section determined by having incident laser at vertical polarization and the signal collection at vertical polarization, (cm^{-1} Sr^{-1})
ρ_v	depolarization ratio, $=Q_{hv}/ Q_{vv}$
$K_{abs,532}$, $K_{abs,266}$	Absorption Coefficient at 532nm and 266 nm respectively
LII	Laser Induced Incandescence
LLS	Laser Light Scattering

1.0 INTRODUCTION

Though appreciable advances have been made in our understanding of the soot formation processes, significant uncertainty remains about the mechanisms leading to the conversion of large Poly Aromatic Hydrocarbons (PAH) into incipient soot particles. Based on previous studies, three possible mechanisms can be identified:

(I) Continual growth of PAH through hydrogen abstraction and acetylene addition (HACA) reactions to large enough sizes that they can be considered as incipient soot particles [1],

(II) Reactive coagulative collisions of large PAH resulting in incipient soot particles (for associated uncertainties, see reference [2]), and

(III) Coagulative collisions of small PAH (mostly 2 ringed compounds) resulting in incipient soot particles followed by a growth process [3].

Though mechanism II is most widely accepted, there is no established experimental evidence to support this theory. Mechanism III on the other hand, is relatively new, and has been postulated based on experimental observations.

All of the above experimental work was performed at Propulsion Engineering Research Center, The Pennsylvania State University

The uncertainties regarding soot inception mainly result due to the experimental difficulties in measuring the concentrations of large hydrocarbons, as well as incipient soot particles. Weiner and Harris [4] have attempted measurement of different sizes of PAH using absorption at various wavelengths. Wersborg and coworkers [5] have used molecular beam sampling to characterize the incipient soot particles. They have shown the formation rates of these particles to be as high as 10^{15} particles/cc/sec with number concentrations of the order of 10^{12} – 10^{13} particles/cc. Recently, D'Alessio and coworkers [3], through their studies on premixed flat flames, have characterized "transparent" particles (transparent because they absorb very little in the visible), which they believe are incipient soot particles. From their studies they have shown these particles to have the following characteristics: i) high depolarization ratio, $\rho_V \approx 0.1$, representative of geometric anisotropy, ii) typically 2 nm in size and ≈ 2500 amu by weight, iii) a fluorescence spectra typical of small PAH (≤2 aromatic rings), i.e., for excitation at 266 nm the fluorescence spectra show a peak in UV ≈ 290 nm, iv) low absorbance which peaks in the UV ≈ 300 nm, v) density ≈ 1.0 gm/cc, vi) complex refractive index m = 1.6-i 0.05 in visible and m = 1.1 - i 0.2 in UV, and vii) infrared spectra indicating these particles to be three dimensional arrangements of 2-ring compounds interconnected by double bonds and aldehyde groups.

In this paper we report our efforts to measure the concentration of these particles in laminar diffusion flames.

2.0 EVALUATION OF ALTERNATE OPTICAL DIAGNOSTICS

Our initial efforts focused in identifying regions of high concentration of incipient particles and subsequent evaluation of various optical diagnostics in measuring their concentrations. A coannular ethene laminar diffusion flame established on a 'Santoro burner' [6] was used for these purposes. The fuel and airflow rates were 3.85 cc/sec and 1060 cc/sec respectively.

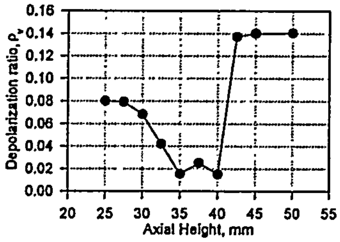


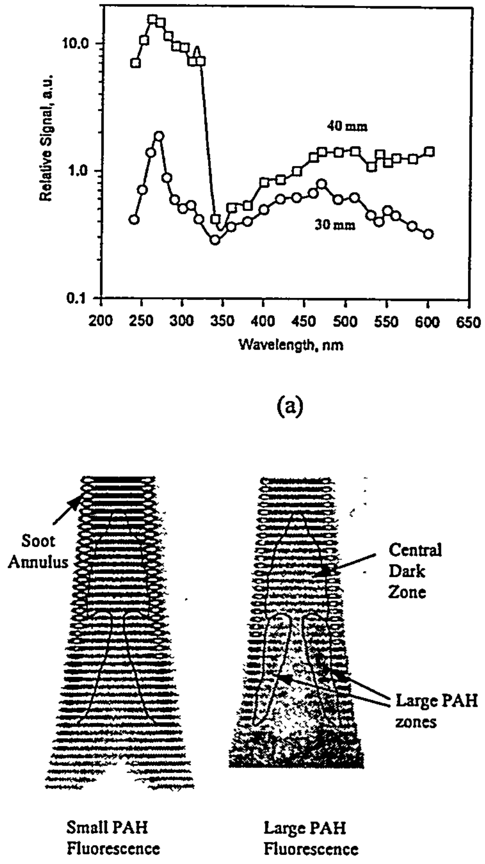
Fig. 1 Depolarization ratio, $\rho_V=(Q_{hv}/Q_{vv})$ values measured along the centerline of ethene 3.85 cc/sec flame; the dip between 30-40 mm height represents evolution of incipient soot from the precursor particles.

2.1 Depolarization Ratio Measurements

The depolarization ratio, $\rho_V=(Q_{hv}/Q_{vv})$, measured along the centerline is shown in fig. 1. Initially, ρ_V has very high values ≈ 0.08 gradually decreasing to ≈ 0.02. This transition was interpreted by D'Alessio as the transformation of the transparent particles into soot agglomerates [3]. However, our present measurements indicate a subsequent increase in ρ_V values in soot laden regions (*c.f.* fig. 1). Similar high ρ_V values were also recorded in the soot laden annular region. Such observations indicate that one cannot distinguish these particles from soot agglomerates merely based on ρ_V measurements.

2.2 Small and Large PAH Fluorescence

Spectral scans of fluorescence (excitation at 266 nm, laser power < 50 μJ/p) at two different heights along the centerline are shown in fig. 2a. While both spectra exhibit a bimodal distribution, the spectra at 30 mm shows a smaller peak in the visible which is typical of the transparent particles [3]. The spectra at 40 mm shows a large peak in the visible (≈480 nm), which is typical of agglomerate soot particles [3].



(a)

(b)

Fig. 2 Fluorescence spectra obtained at two heights along the centerline. Spectra below ≈ 35 mm were similar to the one at 30 mm which has a peak in the UV. Spectra for heights above ≈ 35 mm were similar to the one at 40 mm which shows a second peak in the visible in addition to the one in UV. (b) Stacked line images (2-42 mm) of small (≤2 aromatic rings) PAH and large (2-4 aromatic rings) PAH fluorescence in ethene diffusion flame; a central dark zone appearing in the large PAH fluorescence image marks the region over which precursor particles exist; the head of the boundary of the dark zone also demarcates region of intense small PAH fluorescence (the image on the left).

Two stacked line-images of small PAH fluorescence (excitation at 266 nm, laser power< 50 μJ/p, collection at 295-380 nm) and of large PAH fluorescence (excitation 266 nm, laser power< 50 μJ/p, collection at 500±5 nm) are shown in fig. 2b. A central mushroom head shaped zone, while exhibiting low fluorescence of large PAH species shows unusually high fluorescence of the small PAH. As established through other measurements [7], this zone is coincident with high concentrations of precursor particles. Also, VanderWal and coworkers have come to similar conclusions on parallel arguments [8]. However, the concentration of these particles cannot be established through fluorescence alone, as gas phase small PAH molecules also show similar fluorescence spectra [9].

2.3 LII Signal Falltime / Fluorescence Lifetime Measurements.

As mentioned above, the precursor particles exhibit fluorescence similar to small PAH (≤ 2 aromatic ring) compounds. However, owing to the particulate nature of these species, the ensuing radiation subsequent to laser excitation, need not merely be interpreted as fluorescence signal, but to be having significant contribution from radiant emission due to LII (a possible explanation for the observed increase in signals with laser energy, *c.f.* fig.3.a). VanderWal et al. have come to similar conclusions by varying the excitation laser energy [10]. The measured lifetimes of this fluorescence/LII signal at two laser energies are shown in fig.3b. For small laser energies (<50μJ/P), typical life times were of the order 35 ns. However, when subjected to higher laser energies (>3.6 mJ/pulse), the lifetimes dropped to values less than 25 ns (*c.f.* fig. 3b between 35 and 40 mm heights). This indicates these particles to be highly susceptible to fragmentation when subjected to high power laser radiation. This feature obviates the use of laser diagnostics such as LII which use substantially high laser energies. Furthermore, these particles have high and varying hydrogen content, $X_H \approx$ 0.35 to 0.1 [11], which eliminates the use of laser vaporization techniques, such as, LIF(C_2)LVS [12]. Consequently, the only possible way to measure the concentration of these particles appears to be the use of extinction techniques, which employ low levels of incident radiation.

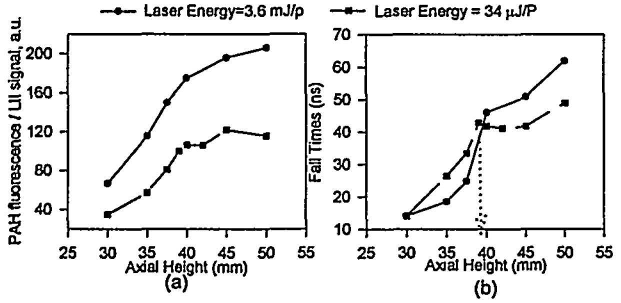


Fig. 3 (a) Fluorescence / emission signal measured along the centerline of the ethene laminar diffusion flame for two different laser energies; excitation at 266 nm. (b) The corresponding fluorescence/LII life times (measured over 128 laser pulses) for the precursor/soot particles. The vertical arrow at 38.5 mm marks the transition from the transparent particles to agglomerate soot particles.

3.0 PRECURSOR PARTICLE CONCENTRATION MEASUREMENTS

One such technique, as suggested by D'Alessio [3], requires the measurement of extinction at two different wavelengths - 266 nm and 532 nm. Subsequently, the volume fraction of soot, f_{vs}, and that of the transparent particles, f_{vp}, can be estimated by solving the equations,

$$K_{abs,532} = \alpha f_{vs} + \beta f_{vp}, \text{ and} \qquad (1)$$

$$K_{abs,266} = \gamma f_{vs} + \delta f_{vp}. \qquad (2)$$

The constants, α-δ, are determined by the optical properties of both soot and the transparent particles. The value of γ used in this study is slightly different from that suggested by D'Alessio et al. [3]. The values used in this study are, $\alpha = 0.8178$, $\beta = 6.827$, $\gamma = 9.132$, and $\delta = 9.320$, with the units of (/μm).

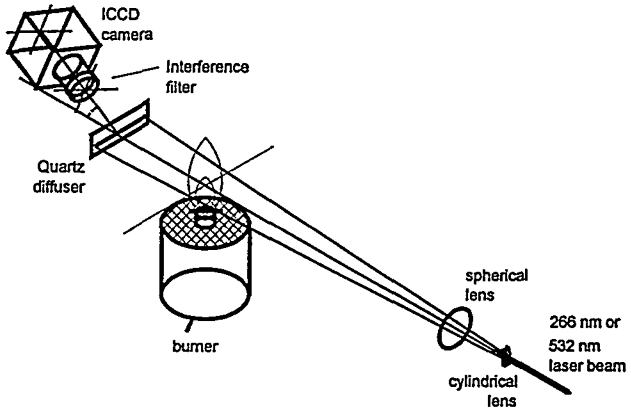


Fig. 4 The experimental setup for extinction measurements. (A brass chimney shielding the laminar diffusion flame is not shown).

3.1 Experimental Setup

The experimental setup used in these measurements is shown in fig. 4. A pulsed Nd:Yag output was expanded as a horizontal sheet by the combination of a quartz cylindrical lens and a quartz spherical lens. The arrangement was to have the focal plane of this combination at the center of a laminar flame established on a 'Santoro burner' [6]. The fuel and the co-annular air flowrates were 3.85 cc/sec and 1060 cc/sec respectively. A one-side-ground quartz plate, 1" x 3" x 1 mm, serving as a screen was imaged by an ICCD camera. The camera was placed at a 30° angle from the horizontal to minimize the amount of laser radiation collected by the camera. This arrangement, while being novel, enables one to record radial extinction profiles without having to move the burner in the radial direction. The radial extinction profiles so gathered were deconvoluted using the 3-pt Abel inversion as suggested by Dasch [13]. The radial profiles of $K_{abs,532}$ and $K_{abs,266}$ were used in eqns. (1) and (2) to obtain radial profiles of f_{vs} and f_{vp}. The values so measured are however prone to errors, especially while measuring low extinction values at 532 nm. These are further accentuated during the tomographic inversion. Hence, there remains a need for the development of a better optical diagnostic.

3.2 Results and Discussion

The f_{vs} radial profiles measured using this technique along with those obtained by using LII [10] are shown in fig.5. Except at low f_{vs} values, there is a good agreement between both the techniques. The most striking feature of the above results is the fact that, these transparent particles exist in appreciable quantities, with f_{vp} being of the same order of magnitude as f_{vs}. Also, this study clearly shows the formation of these particles over a broad region in addition to that along the centerline (*c.f.* fig.6) as previously observed by Dobbins et al. [7].

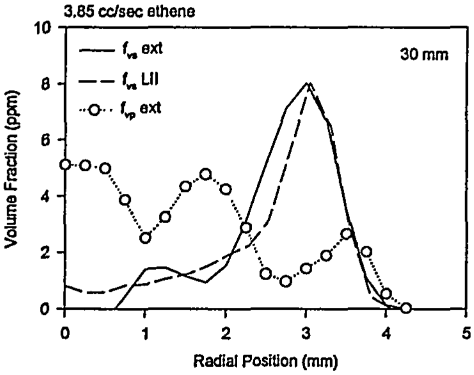


Fig. 5 Comparison between the f_{VS} radial profiles measured using extinction and LII. Also, the corresponding f_{Vp} profile is shown.

Additionally, low in the flame, these particles are concentrated more towards the fuel rich central core. At higher locations, wide regions could be found where these particles co-exist along with soot. Also, minute traces of these particles could be observed on the oxidizer side of the soot annulus. However, due to the errors associated with the extinction technique, this could not be ascertained.

3.3 Measurements in Low-Sooting Flames

Similar extinction measurements were performed in a low sooting ethene + methanol flame (ethene 3.302 cc/sec + methanol 1.096 cc/sec). Previous studies indicate substantial reductions in small and large PAH fluorescence in addition to similar reductions in f_{vs} values [15]. However, the present extinction measurements show no such reductions in f_{vp} (*c.f.* fig.7). Having given due consideration to the errors introduced by uncertainties in the optical constants, one cannot still explain such observations based on the notion of soot evolution as suggested by D'Alessio et al., wherein it is believed that inception occurs by coagulative collisions of small PAH. In fact, Miller et al. have shown the concentrations and rates of small PAH to be so small that inception rates cannot be attributed solely to their coagulative collisions with subsequent dimerization [16]. While the current observations suggest newer and additional mechanisms associated with soot inception, this could not be ascertained considering the limited scope of the present study.

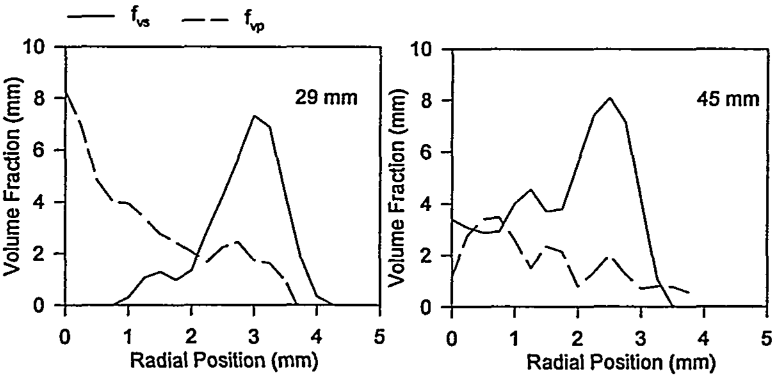


Fig. 6. f_{VS} and f_{Vp} radial profiles measured at two axial positions.

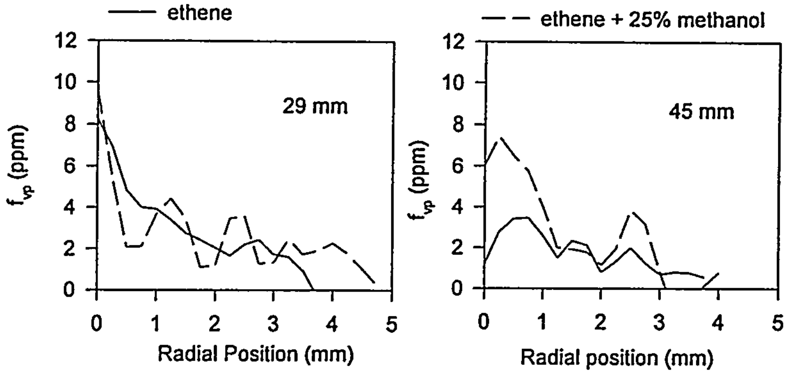


Fig. 7 f_{vp} radial profiles at two different heights measured in ethene and ethene+25% methanol flame.

4.0 CONCLUSIONS

This study confirms the existence of transparent particles in laminar diffusion flames, which recently have been identified to exist during the soot formation process in premixed flames. In agreement with previous findings, these particles were found to exhibit high depolarization ratio values and fluorescence similar to small PAH species. However, neither of these characteristics could be advantageously used in measuring their concentrations.

These particles were found to be susceptible to fragmentation upon the incidence of moderate laser energies (~3.6 mJ/P). This characteristic obviates the use of high laser energy techniques in the measurement of their concentration. This limits our choices to low energy optical techniques such as extinction.

A novel extinction technique, following the rules set forth by D'Alessio, was employed in measuring the volume fractions of these particles in a laminar diffusion flame. At lower heights, these particles were found to be concentrated in the fuel rich core, while at higher locations, these particles could be found with appreciable concentrations even in the soot laden regions. The most surprising result of this study was the abundance of these particles, with volume fractions comparable to those of soot.

Having given due consideration for various channels of error propagation – those due to low values of extinction (especially at 532 nm), those due to tomographic inversion, and those introduced by uncertainty in the optical properties - measurements were performed in a low sooting ethene + methanol laminar diffusion flame. They showed very little change in the f_{vp} values, even though significant reductions in PAH fluorescence and f_{vs} could be observed as compared to those in a pure ethene diffusion flame. Such observations raise questions regarding the nature of participation of these particles in soot formation. On the other hand, it is plausible to question the accuracy achieved through the current technique. However, further validation is not possible, as there is no physical sampling technique currently available with high enough spatial resolution. Also, considering the highly reactive nature and varying composition of these particles, it is plausible that the optical properties could be varying with residence time. The present measurements reflect a first step towards developing a non-intrusive optical diagnostic for measurement of these particles.

Also, future studies should concentrate on estimating the size and number density information of these particles. One could follow guidelines set forth by D'Alessio in such an endeavor. Our initial efforts in this direction indicate that the optical constants suggested by D'Alessio are subject to doubt and that they need to be reevaluated. Furthermore, the criteria for the formation of these particles, such as, temperature, stoichiometry, etc., need to be investigated.

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