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# Soot Precursor Formation and Limitations of the Stabilomer Grid

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Colloquium: SOOT, PAH AND OTHER LARGE MOLECULES

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| | |
|---|---|
| Abstract | 226 |
| Introduction | 693 |
| Experimental Details | 455 |
| Simulation Details | 396 |
| Results and Discussion | 1464 |
| Conclusion | 298 |
| Acknowledgements | 113 |
| 39 References | 717 |
| 5 Figures (244+746+161+162+173) | 1486 |
| Total (excluding abstract) | 5622 |

## Abstract:

We have performed flame-sampling aerosol mass spectrometry with vacuum-ultraviolet photoionization of an Ar-diluted $C_2H_2/O_2$ flame using a near-atmospheric pressure (700 Torr) opposed-flow burner. We recorded aerosol mass spectra at different distances from the fuel outlet for fixed ionization energies and in a fixed position while tuning the photoionization energy. Recorded mass spectra contain a wide variety of peaks, highlighting the importance of small building blocks and showing a variety of chemical species that extends beyond the traditional classification of PAH species based on thermodynamic stability. In addition, we performed stochastic simulations of PAH growth in the flame in order to elucidate the chemical composition of species associated with peaks in the measured mass spectra. These simulations were conducted using a stochastic nanoparticle simulator (SNAPS). Synthesis of experimental and simulated results showed that peaks in the observed mass spectra generally consisted of a mixture of PAH isomers. At m/z = 154 and 202, for example, experiments and simulations suggested that additional isomers than biphenyl and pyrene are important. Furthermore, the results highlight the importance of odd-carbon numbered species and complex growth paths. It is clear from the experimental results that species of higher masses can build up concentration ahead of species of lower masses. Our experimental results show, for example, that the peak at m/z = 278 appears ahead of the peak at m/z = 202.

Keywords: Soot, Mass Spectrometry, Modeling, Acetylene, PAH

## 1. Introduction

Combustion processes are major sources of hazardous airborne pollutants, including polycyclic aromatic hydrocarbons (PAHs) and soot. However, there is a very poor understanding of the chemical pathways governing molecular growth from light gaseous species to large PAH molecules and soot particles [1-3]. Production of large PAHs and soot is believed to be controlled by the formation of small aromatic species, containing one to a few rings [1,2,4,5]. Hence, the formation of the first aromatic ring, i.e., benzene, has been widely studied in different flames, see, e.g., [6-11].

Developing a comprehensive description of soot formation will require an understanding of the chemistry of molecular growth beyond the first aromatic ring and identification of key intermediates. One important mechanism proposed for hydrocarbon-growth chemistry is hydrogen abstraction from the reacting hydrocarbon by a free hydrogen atom, followed by acetylene ($C_2H_2$) addition to the hydrocarbon radical site, i.e., the so-called HACA mechanism [5,12]. Under some conditions, however, the HACA mechanism does not appear to be able to describe observed hydrocarbon growth. Keller and co-workers [13] concluded that the HACA mechanism does not promote growth of large PAHs. This growth may be explained by unimolecular reactions leading to the formation of PAHs with bays and coves. The HACA mechanism has also been reported to be too slow to account for experimentally observed growth rates; see, e.g., the works by Violi’s group [14,15].

Other suggested growth paths include addition of methyl ($CH_3$) [16], vinyl ($C_2H_3$) [17], and phenyl ($C_6H_5$) [18] radicals. Some studies have stressed the role of the propargyl ($C_3H_3$) recombination reaction in the formation of the first aromatic ring [2,10,19]. Propargyl and vinylacetylene ($C_4H_4$) have also been included in growth mechanisms leading to the formation of the second aromatic ring to produce naphthalene [20]. Shukla and Koshi [17,21,22] concluded that several growth pathways should be incorporated in the construction of mechanisms aimed at describing wide ranges of combustion conditions.

Mass spectrometry is a measurement approach that can provide some insight into the chemistry leading to PAH and soot formation [23]. Various setups, using different ionization sources, have been successfully applied for detection and characterization of molecules up to masses of a few hundred u. Öktem et al. [24] combined mass spectrometry, scanning mobility particle sizing, and transmission electron microscopy in a flat premixed ethylene/oxygen/argon flame. They found support for aromatics dominating early growth stages, whereas aliphatics contributed significantly at later stages.

Faccinetto et al. [25] observed two manifolds of peaks when they studied mass spectra from deposits on absorbing filters in the soot inception region of a low-pressure premixed methane/oxygen/nitrogen flame. The high-mass peak was attributed to PAHs with carbon numbers from 30 to 62, and the authors suggested the formation of large PAHs to be related to the formation of the first soot particles. Keller et al. [13] also observed a second manifold in this mass range. However, this second manifold of peaks was not observed in the recent work by Skeen et al. [26], in which particles sampled from opposed-flow flames of acetylene/oxygen/argon, ethylene/oxygen/argon, and propane/oxygen/argon were focused onto a copper target. The target was heated to ~550-650 K to vaporize volatile species in the particles. Skeen et al. [26], however, observed species with ionization energies higher than what is expected from the thermodynamically most stable isomers identified by Stein and Fahr [27]. This finding provides evidence for the importance of kinetics as opposed to thermodynamic stability for molecular growth mechanisms. The current study should be viewed as a continuation of the work published by Skeen et al. [26], and it aims to characterize soot precursors in the mass range of ~78-250 u, using a combined experimental and simulation approach. Synthesis of experimental and simulated observations elucidated the chemical composition of prominent masses in this range and demonstrated that peaks in the mass spectra generally consisted of a mixture of PAH isomers. Importantly, both experiments and simulation showed a variety of chemical species that extends beyond the traditional classification of PAH species based on thermodynamic stability. Consequently, this work represents a significant step in building a more accurate and comprehensive understanding of PAH growth and will greatly benefit further study of soot formation.

## 2. Experimental Details

The experimental setup has been described elsewhere [26], and a detailed description will not be provided here. Briefly, a non-premixed, opposed-flow burner is enclosed in a chamber maintained at 700 Torr. The two sides of the opposed-flow burner were separated by 14 mm. Ar-diluted $C_2H_2$ gas (0.0021 g $cm^{-2}$ $s^{-1}$ $C_2H_2$ and 0.0347 g $cm^{-2}$ $s^{-1}$ Ar) was supplied through a 14-mm ID tube on the fuel side, and Ar-diluted $O_2$ (0.0053 g $cm^{-2}$ $s^{-1}$ $O_2$ and 0.0232 g $cm^{-2}$ $s^{-1}$ Ar) passed through an identical tube on the oxidizer side. The fuel and oxidizer tubes are surrounded by outer tubes of 20-mm ID, through which Ar shielding flows help stabilize the flame. The resulting soot-formation flame was greenish with a thin orange layer close to the fuel outlet side. The maximum (radiation corrected) flame temperature, measured using a fine-wire Type-B thermocouple, was about 2100 K.

Intermediates were sampled along the vertical centerline of the flame using a horizontally positioned quartz microprobe with a tapered tip of 180 μm ID and maximum OD of 3 mm. The probe assembly is disconnected from the burner assembly, and, in order to sample from different heights in the flames, the burner assembly is translated vertically while the probe is kept fixed. The uncertainty in these vertical translations is considered to be within ± 0.25 mm.

Sample gas and particles entered an aerodynamic lens system [28-30], which focused the particles into a beam. The particle beam hit a copper target, which was heated to roughly 575 K and located inside a low-pressure chamber. The background pressure inside this chamber was on the order of $10^{-8}$ Torr. It is believed that particle coagulation and gas-phase nucleation and condensation occurred either during the interaction with the microprobe used to extract particles and gases from the flame or during the sample expansion into the sampling line before the aerodynamic lens system. This physical growth is, however, considered favorable since the aerodynamic lens system does not focus gas-phase species or small particles (<~50 nm). We assume that most chemical reactions are quenched during sample extraction and have a negligible effect on measured signals and that masses observed correspond to structures present at the sampling point in the flame.

Semi-volatile species vaporize from the heated copper block and are then photoionized using tunable (7.4-10.5 eV) vacuum ultraviolet (VUV) radiation, generated at the Advanced Light Source synchrotron facility at Lawrence Berkeley National Laboratory. The molecular ions generated are pulse extracted into the time-of flight tube of a mass spectrometer at a rate of 15 kHz. Ions emerging from the flight tube are detected on a microchannel-plate detector, and mass spectra are recorded using a multichannel scaler. The mass resolution is approximately 2000.

## 3. Simulation Details

Stochastic simulation of PAH growth in the acetylene flame was performed in order to elucidate the chemical composition of species associated with peaks in the measured mass spectra. These simulations were conducted using SNAPS (Stochastic Nanoparticle Simulator), a recently developed software for simulating gas-phase nanoparticle growth. SNAPS, along with an accompanying PAH chemical-growth mechanism, has been described in detail elsewhere [31]. Briefly, SNAPS uses an algorithm based on kinetic Monte Carlo to generate stochastic trajectories of the growth of an initial “seed” molecule in a gas-phase environment, governed by a given reaction mechanism. A PAH-growth model was formulated and includes addition of major proposed PAH-growth pathways, including HACA, addition of ethylene and benzene, and addition of vinyl, methyl, propargyl, cyclopentadienyl, and phenyl radicals. Additionally, SNAPS requires inputs that describe the combustion environment, namely temperature and ambient gas-phase species, such as H radicals or acetylene. These inputs were computed using the OPPDIF program in CHEMKIN [32] and the ABF chemical mechanism [33]. Because the formation of the first aromatic ring is considered to be the first step of PAH formation, benzene and toluene were chosen as the even- and odd-numbered C-atom seed molecules for simulations. Furthermore, these molecules were among the most abundant single-ring aromatic species based on the experimentally recorded mass spectra. SNAPS was then used to model the growth of molecules as they travel from the fuel outlet towards the flame front along the center streamline of the apparatus. Ensembles of such trajectories were used to characterize PAH chemical composition and growth.

SNAPS simulations were analyzed to classify the most important PAH structures for specific mass ranges. To simplify analysis of the vast amount of potential structures, PAHs were classified by carbon configuration using social permutation invariant topological (SPRINT) coordinates [34], which utilize graph theory to describe the connectivity of an isomer. SPRINT coordinates were computed for each SNAPS trajectory. Importantly, PAHs with equivalent connectivity will have almost identical SPRINT coordinates, which are invariant under all permutations of a set of N atoms. Isomers with specific carbon numbers were grouped, focusing specifically on carbon-carbon connectivity, by placing a limit on the *p*-2 norm of the difference between the vectors representing the SPRINT coordinates of each pair of PAHs in the target ensemble. This *p*-2 norm threshold was adjusted to produce distinct carbon configurations for the top five most frequently observed PAH structures.

## 4. Results and Discussion

Figure 1a displays a typical mass spectrum for mass-to-charge ratios (m/z) between 75 and 350 at a distance from the fuel outlet (DFFO) of 5.75 mm, i.e., where the signal in this m/z range peaks. Throughout this paper, singly ionized molecules are assumed to be the only important contributors to the observed signal. Figure 1b shows the simulated mass spectrum at DFFO = 5.75 mm, which was computed using a weighted average of 2000 each of benzene-seed and toluene-seed trajectories. These seeds were considered to begin growth at a height of approximately 5.5 mm, which approximately locates the maximum rate of production of H radicals and was considered to be the beginning of the main chemical-reaction zone favorable to PAH growth. At this height, based on the experimental mass spectra for the acetylene flame, the concentration of toluene was estimated to be approximately half that of benzene. This estimation was based on the assumption that structures providing signal at m/z = 91 originated from the structures at m/z = 92 and had undergone hydrogen abstraction around the microprobe and in the sampling line. This 2:1 ratio was used to compute the mass distribution in Fig. 1b, which agrees well with the trend of the measured mass spectrum (Fig. 1a).

The number of carbon atoms in each cluster of peaks is known for the simulated mass spectrum, and we have estimated this number for the experimental spectrum. The cluster starting around m/z = 226 is estimated to have 18 carbon atoms, and the cluster beginning at approximately m/z = 300 is estimated to have 24 carbon atoms. Assigning a carbon number ($n_C$) to each cluster allows us to correct for contributions from $^{13}C$, which has been done to the experimental spectrum in Fig. 1. Some of these peaks may contain oxygenated species, however, thus reducing the number of carbon atoms to a number below the integer assigned to that cluster.

Figure 1a demonstrates that clusters assigned odd carbon numbers yield weaker signals than clusters assigned even numbers. This behavior is reproduced in the simulated spectrum in Fig. 1b. Peaks associated with an even number of carbon atoms (e.g., masses of approximately 202, 226, 252) in the simulated mass spectrum can be traced to benzene-seed trajectories, whereas those associated with odd carbon number (e.g., masses of approximately 214, 232, 264) can be traced to toluene-seed trajectories. This result is not surprising considering that acetylene was the most commonly added species in the model. Although the SNAPS PAH-growth mechanism includes methyl addition, and methyl is the second most commonly added species, it is limited by available chemical rates in the literature. The current prevalence of odd numbered carbon atoms, therefore, may indicate that additional exploration is needed for PAH-reaction pathways involving methyl radicals.

Although the stabilomer grid presented by Stein and Fahr [27] could potentially explain the prevalence of many of the even-carbon numbered peaks in Fig. 1, it does not fully explain the variety of prominent peaks observed. For example, in the cluster of peaks stemming from species believed to have $n_C = 22$, the stabilomer grid predicts two species with molecular formulas $C_{22}H_{10}$ and $C_{22}H_{12}$. The peak corresponding to the mass of $C_{22}H_{12}$ is strong. However, the peak with mass corresponding to $C_{22}H_{10}$ is weak in the experimental mass spectrum whereas the peaks at masses corresponding to $C_{22}H_{14}$ and $C_{22}H_{16}$ are relatively strong. Furthermore, the groups with $n_C = 24$ and $n_C = 26$ show only weak peaks corresponding to 10 hydrogen atoms, whereas the stabilomer grid suggests that these peaks should be strong. Peaks corresponding to 12, 14, 16, 18, and 20 hydrogen atoms are all stronger than the peaks corresponding to 10 hydrogen atoms for these two clusters. Apart from $C_{24}H_{10}$ and $C_{26}H_{10}$, the stabilomers for $n_C = 24$ and 26 contain species with 12 and 14 hydrogen atoms. Hydrogen addition around the microprobe and in the sampling line could potentially explain a one or two hydrogen atom difference between observed masses and those listed in the stabilomer grid. However, we consider a difference of four hydrogen atoms or more to be significant. In addition, no obvious signs of hydrogen abstraction are seen if the stabilomer grid is used for structural interpretation of observed peaks. Furthermore, the stabilomer grid does not explain the peaks of odd carbon numbers. For instance, the clusters with $n_C = 19$ and $n_C = 21$ are almost as strong as neighboring even-numbered clusters. However, Stein and Fahr [27] pointed out that kinetic factors most likely determine carbon polymerization below 1500 K.

SNAPS simulations provided molecular structures associated with mass-distribution peaks. Figure 2 shows the most commonly observed structures for $n_C$ between 12 and 18 according to the model. These structures account for the cluster of masses associated with peaks that differ by hydrogen content. These hydrogen atoms were neglected to focus specifically on carbon structure, as some hydrogen addition or abstraction may occur within the sampling line. Measuring the photoionization (PIE) curves can sometimes provide conclusive evidence on isomer composition, but it is difficult for larger species [23]. In order to estimate the contributions of different isomers to individual mass peaks, we fit PIE curves using estimated or measured photoionization cross sections convolved with a Gaussian energy distribution with a full width at half max (FWHM) of 0.59 eV.

The ionization thresholds and shapes of the recorded PIE curves at $m/z = 78$ and $m/z = 92$ suggest that benzene and toluene, respectively, dominate in these two mass channels at the DFFO studied (7.0 mm). The photoionization cross section for benzene was obtained from Ref. [35], and, for toluene, the ionization cross section reported by Zhou et al. [36] was used.

Figure 3 shows the PIE curve recorded at $m/z = 154$ at DFFO = 7.0 mm. Also shown is the fitted curve using the estimated ionization-cross section curves of biphenyl and 1-vinylnaphthalene, both taken from

Ref. [37]. The contribution from 1-vinylnaphthalene appears to be significant. However, the estimated ionization cross-section curve of acenaphthene [37] is very similar to that of 1-vinylnaphthalene, and, hence, acenaphthene cannot be ruled out as an important isomer. These results agree well with the simulated results. For $n_C = 12$, the most common isomer obtained from the simulations is an acenaphthylene structure, followed by a 1-vinylnapthalene structure (see Fig. 2). Although acenaphthylene has a mass of 152 u, hydrogenation of the double bond in the 5-membered ring, as in the migration pathway suggested by Frenklach et al. [38], can lead to acenaphthene, which has a mass of 154 u. Nevertheless, the model does not predict biphenyl to be among the five most common isomers for $n_C = 12$, even though biphenyl is listed in the stabilomer grid.

At m/z = 202, pyrene is the most thermodynamically stable isomer [27]. However, its photoionization efficiency curve from Ref. [37], although only estimated, does not resemble the recorded PIE curve, which looks fundamentally different (see Fig. 4). This observation is consistent with the simulations, where pyrene was only observed with a frequency of 0.5%. Instead, the simulation results show a much wider variety of potential PAH species. In particular, the structures show the importance of 5-membered rings, which are prevalent throughout the classified structures. The most commonly observed structure ($n_C = 16$, Fig. 2, column A) contains 5-membered rings and was also identified as a stabilomer by Stein and Fahr [27]. The dominance of acetylene addition is reflected in the most commonly observed structures from $n_C = 12$ to $n_C = 18$, which can be viewed as a sequence of structures growing via addition of acetylene. These simulation results demonstrate the importance of the existing HACA-growth mechanism, but also suggest avenues for further exploration, namely reactions involving 5-membered rings. The importance of 5-membered rings is consistent with the recent conclusions of Kislov et al. [39], who found a preferential formation of 5- rather than 6-membered rings based on theoretical kinetic arguments.

A simple mass progression for which species of lighter masses are first formed and then followed by species of higher masses does not explain the results recorded in the $C_2H_2$ flame. Figure 5, for instance, shows the ion signal at m/z = 202 and m/z = 278 as functions of the DFFO. The figure illustrates that the peak at m/z = 278 rises ahead of (i.e., is higher at smaller DFFOs than) the peak at m/z = 202. Another example is that the peak at m/z = 266 ($n_C$ = 21) appears ahead of the peaks at m/z = 202 and 165. More work is needed to determine whether high-mass peaks forming ahead of low-mass peaks belong to different growth-path branches than their slower growing low-mass peaks. The result, however, indicates that HACA alone cannot describe the chemical growth of PAHs.

## 4. Conclusions

We performed flame-sampling aerosol mass spectrometry studies with vacuum-ultraviolet photoionization of a near-atmospheric pressure (700 Torr) Ar-diluted $C_2H_2/O_2$ flame using an opposed-flow burner. We recorded aerosol mass spectra at different distances from the fuel outlet for fixed ionization energies and in a fixed position while tuning the photoionization energy between 7.4 and 10.5 eV. We learned that recorded mass spectra contain a wide variety of peaks, highlighting the importance of small building blocks and species that extend beyond the classification of PAHs based on thermodynamic stability.

In addition, we performed stochastic simulations of PAH growth in order to elucidate the chemical composition of species associated with peaks in the measured mass spectra. These simulations were conducted using SNAPS. The simulated mass distribution qualitatively agrees well with experiment.

The stabilomer grid presented by Stein and Fahr [27] does not provide a satisfactory picture of the observed mass spectra, even though the stabilomer grid predicts hydrocarbon isomers with masses for which experimental signal is often significant. However, the current results show it is often incorrect to ascribe observed peaks to single isomers, and kinetic factors need to be considered. At m/z = 154 and 202, both experiments and simulations suggested that other isomers than biphenyl and pyrene are important. Experimental conclusions are, however, to a large extent based on estimated photoionization efficiency curves due to a lack of measured ones. Furthermore, the results highlight the importance of odd-carbon numbered species and complex growth paths. It is clear that species of higher masses can build up concentration ahead of species of lower masses. Our experimental results show, for example, that the peak at m/z = 278 rises ahead of the peak at m/z = 202, the latter corresponding to the mass at which pyrene is expected to be present.

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## List of Figures

Fig. 1. a) Experimental mass spectrum recorded at DFFO = 5.75 mm. b) Calculated mass spectrum from the simulated results at DFFO = 5.75 mm. The strongest peak is normalized to 1.