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FLEXOELECTRICITY AND THE ELECTRICAL ASPECTS OF CARBON FORMATION IN FLAMES

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Introduction

Flexoelectricity is found in carbon materials where a local strain gradient caused by curvature of the graphene network induces an electric polarisation. The flexoelectric effect has been explored in carbon nanocones,[1] and we recently extended this analysis to hydrogen terminated polycyclic aromatic hydrocarbons (PAH).[2] We found that a simple description based on the local pyramidalization angle predicts this effect well in PAH and have been developing an anisotropic forcefield description to understand how this polarisation impacts these materials. Of particular interest is the impact of polar aromatics on flame-generated carbonaceous particles such as soot and carbon black. These curved PAH (cPAH) have long been thought to be involved in this process with corannulene being extracted from soot and certain flames able to form completely closed fullerenes. We have recently demonstrated using molecular dynamics simulations that the nucleation rate can be increased for cPAH in the presence of ionic species, whereas no impact was found for flat PAH. This leads us to explore whether these species are found in early carbonaceous nanoparticles.

In this work, we make use of electron microscopy, fringe analysis, and multislice simulations to quantify the degree of curvature in early flame nanoparticles. We then use electronic structure methods to explore these cPAH polarisations, stability and interactions with ions.

Methods

Carbon nanoparticles were sampled thermophoretically from an ethylene coflow diffusion flame. The JEOL 2100F TEM was used with an accelerating voltage of 200 kV. Electronic structure calculations were performed using the Gaussian 09 software using the dispersion corrected hybrid density functional B97D/6-311G(d,p)// B97D/cc-pVTZ.

Results and Discussion

Figure 1 shows two electron micrographs from the lowest height above the burner (HAB) that we sampled, 10 mm and at the tip of the flame, 49 mm. By analysing 209 primary particles we were able to build up statistics to quantify this curvature using the tortuosity. The lowest HAB fringes had tortuosity values of 1.18-1.20 while at 49 mm the tortuosity decreased to 1.15-1.17 with fringe

lengths with a median value of 0.9-1.05 nm. We then simulated three curved PAH with 1, 2, and 3 pentagonal rings, with fringe length of ~1 nm. We found that for the low height above the burner the tortuosity values indicated 1-2 pentagons were integrated in 62.5% of the fringes.

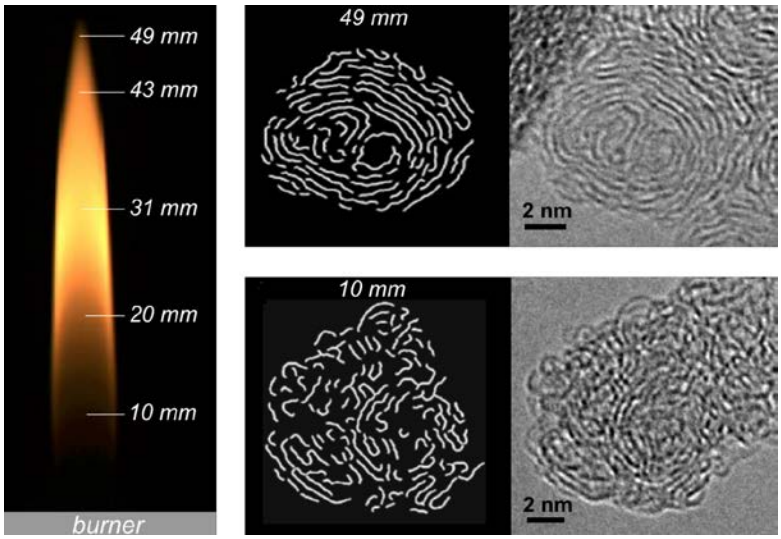

Figure 1. Two electron micrographs of small soot primary particles at a low and high height above the burner.

Performing electronic structure calculations on the two pentagon-containing cPAH we found a strong dipole moment of 5.32 D. The persistence of the dipole was estimated from the rate of inversion and found to be stable during the milliseconds over which soot inception occurs. Strong interactions were computed between chemi-ions and this curved species (-150-170 kJ/mol) due to the ion-dipole interactions able to stabilise a small cluster of four cPAH. We finally performed quantum molecular dynamics simulations on the cPAH chemi-ion system. We were able to confirm the persistence of the dipole moment varying only by +-0.5-1 debye. The chemi-ion was found to interact strongly with the cPAH on the rim and pentagonal site over 2 ps.

Conclusions

Electron microscopy of early combustion-generated nanoparticles indicates strongly polarised molecules. Calculations revealed their ability to interact with chemi-ions in the flame.

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