Numerical simulation and parametric sensitivity study of optical band gap in a laminar co-flow ethylene diffusion flame

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ABSTRACT

A detailed population balance model is used to perform a parametric sensitivity study on the computed optical band gap (OBG) of polycyclic aromatic hydrocarbons (PAHs) in a laminar co-flow ethylene diffusion flame. Assuming that the OBG of PAHs in soot can be estimated by the energy difference between the highest occupied and lowest unoccupied molecular orbitals in single PAHs, OBG may be correlated with the number of aromatic rings in PAHs. This allows insights into which are the key species involved in the formation of soot. PAH size distributions are computed along the centreline and in the wings of the flame. We compare our simulations with experimentally determined soot volume fraction and OBG (derived from extinction measurements) from the literature. It is shown that the model predicts reasonably well the soot volume fraction and OBG throughout the flame. We find that the computed OBG is most sensitive to the size of the smallest PAH which is assumed to contribute to the OBG. The best results are obtained accounting for PAH contribution in both gas and particle phases assuming a minimum size of ovalene (10 rings). This suggests that the extinction measurements show a significant absorption by PAHs in the gas phase at the visible wavelength that is used, which has been demonstrated by experiments in the literature. It is further shown that PAH size distributions along the centreline and in the wings are unimodal at larger heights above burner. Despite the different soot particle histories and residence times in the flame, the PAH size associated with both modes are similar which is consistent with the near-constant OBG that is observed experimentally. The simulations indicate that the transition from the gas phase to soot particles begins with PAHs with as few as 16 aromatic rings, which is consistent with experimental observations reported in the literature.

1. Introduction

Particle inception is the least understood process of soot formation in hydrocarbon combustion. It is widely accepted that the gaseous precursors to solid soot particles are polycyclic aromatic hydrocarbons (PAHs) [1–4]. These PAHs grow in size due to chemical reactions and then stick. Experimental evidence for the sticking of PAH comes, for example, from the laser ionisation mass spectrometric study by Happold et al. [5]. Masses of molecular fragments ablated from soot in a 100-Torr ethylene–oxygen flame display a periodicity of about 450 amu. Combined with the quantum mechanical calculations [6] and Bragg reflexions [7] reported in the literature, these studies provide support that nascent soot is made up of stacks of PAHs. The next question that arises is at what point do PAHs stick? A systematic effort has been made in this direction using a variety of experimental techniques. The rapid insertion technique has been routinely employed (see, e.g., [8–11]) to collect particles which can be subjected to ex situ analysis using Raman spectroscopy [12–14] and high resolution transmission electron microscopy (HRTEM) [13,15] to characterise the crystalline structure of soot particles. Observed Raman signals

for soot generated from a non-premixed ethylene/air flame, which interestingly only show a slight variation, are attributed to particulates with a crystallite length of 1.0–1.2 nm, or PAHs which are 4–5 rings across [12]. HRTEMs of soot in ethylene and benzene-air flames reveal structures composed of sheet-like PAH molecules referred to as lattice fringes [13]. The most common fringe length throughout either flame is found to be equivalent to the length of a PAH about 4 rings across. However, these techniques only reveal the length of the crystallite structures. In Ref. [16] an entirely different approach is used where visible light extinction measurements in a series of non-premixed ethylene/air flames of varying dilution ratios are performed and used to determine the optical band gap (OBG) as a function of flame position which is then related to the number of aromatic rings in a PAH [17]. The observed OBG is found to correspond on average to a PAH consisting of about 14 aromatic rings [16].

Tauc et al. [18] related the absorption behaviour of Germanium to the OBG, the energy required for an electronic transition between the top of the valence band and the bottom of the conduction band. The absorption edge of amorphous Germanium is described by the relation:

$$\alpha h\nu \approx (h\nu - E_g)^r, \tag{1}$$

where α is the absorption coefficient, $h\nu$ is the photon energy, E_g is the OBG and r is a constant related to the band structure. In amorphous semiconductors r is taken to be 2 for a nondirect transition. In crystalline semiconductors r describes both the directness and the allowedness of the transition. For the experimental results referenced in this work $r = 1/2$ for a direct allowed transition is utilised. A plot of $(\alpha h\nu)^{1/r}$ against $h\nu$ has a distinct linear regime; therefore, extrapolation of this region to the abscissa yields the OBG. Robertson and O'Reilly [19] showed that the OBG scales inversely with $M^{1/2}$, where M is the number of aromatic rings in a PAH. By calculating the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO–LUMO) gaps for a series of PAH molecules and fitting the results [17] to the relationship proposed by Robertson and O'Reilly [19], the following relationship is obtained:

$$E_g = \frac{5.8076}{M^{1/2}} + 0.5413. \tag{2}$$

Through this relationship the OBG derived from extinction measurements can be related to the number of aromatic rings in a PAH. While this relationship can in principle be applied to any flame, it is assumed that nascent soot particles are dominated by clusters of moderately sized PAHs and that the OBG can be estimated by the HOMO–LUMO gaps of single PAHs [17]. However, it has been shown that the stacking of PAHs increases the density of states near the OBG [6] which causes a decrease in the HOMO–LUMO gap [20] and is revealed as a lowering of the OBG [14,21]. Also, the spectral range used in the fit of the OBG may be more heavily influenced by the larger PAHs in the particle [17,20]. We make no attempt here of addressing these issues, which are beyond the scope of the present paper.

In modelling studies of soot particle dynamics the growth of PAHs up to infinite size can be modelled via H-abstraction-C_2H_2-addition reactions (HACA) [1,22,23], or in combination with the more recently proposed PAH-addition cyclisation, phenyl addition cyclisation and methyl addition cyclisation mechanisms (see Ref. [24] and references therein), deterministically solving for the concentration of each PAH species is computationally intractable. There are other detailed models of soot formation and solution methods. Kraft and co-workers employ a detailed population balance model which is solved using a stochastic numerical method. The model describes particles as aggregates composed of primary particles which are in turn composed of individual PAHs, thus containing information on particle size, morphology, and the internal

structure of the particles. The exact structure of each PAH is resolved; therefore, the exact number of aromatic rings in each PAH is known. The OBG can then be computed using Eq. (2) and compared with experimentally determined OBG. The model has been used to simulate the oxidation of soot by NO [25]. It is found that a number of N and O atoms on the PAH edge cannot be removed, specifically, those on phenalene-like structures. This indicates that the present mechanism for PAH oxidation requires some phenalene removal process to improve model predictions of soot oxidation. The stochastic approach has also been used to understand the collision efficiency of the sticking of PAHs, where computed mass spectra are compared with the experimental mass spectra of Happold et al. [26] which contain distinctive features resembling PAH monomers and dimers. A unique feature of the model is that it resolves the size and connectivity of the primary particles in an aggregate; therefore, TEM-like projections of aggregates can be produced to visualise the temporal evolution of the fractal dimension in different flames [27]. Investigations of soot particle size distribution functions, morphology and composition have been performed in the context of engines [28]. The stochastic approach is also used to follow the morphology of aerosols in Titan's atmosphere [29] and to study the sintering of titania, silica and silicon.

The purpose of this paper is to compare computed OBG with OBG derived from extinction measurements made in a laminar co-flow ethylene diffusion flame [16], to understand the implications on the critical PAH size for soot inception, and to add jump processes to the kinetic Monte Carlo-aromatic site (KMC-ARS) submodel. The flame chemistry and structure are taken from Herdman et al. [12] who employ an axisymmetric model which solves the full set of transport equations and we apply a soot population balance model in a post-processing step. A parametric sensitivity study is carried out to understand how key model parameters impact the OBG quantitatively and to aid in the interpretation of the OBG.

The paper is organised as follows: Section 2 introduces the computational method. Section 3 introduces key aspects of the detailed population balance model, and the jump processes that are added to the KMC-ARS submodel. Section 4 contains a description of the direct simulation algorithm (DSA) used in this work and the changes that are made to the algorithm. Sections 5.1 and 5.2 present the soot volume fraction and OBG, respectively. Section 5.3 presents the parametric sensitivity study of the computed OBG. Lastly, implications on the underlying simulations are discussed in Section 6.

2. Computational method

The computational method consists of two parts. In the first part, velocity, species and temperature fields for a laminar co-flow ethylene diffusion flame are taken from Herdman et al. [12]. They employ an axisymmetric model which has been developed by Smooke and co-workers [30–34] which solves the full set of mass, momentum, species and energy equations as well as the soot transport equations using a sectional representation of the soot particle size distribution [35]. A gas-phase chemical mechanism, and species thermodynamic and transport properties are supplied as input. The transport equations of the discretised particle size distribution function are solved to approximately account for the production and consumption of key gas-phase species due to inception, condensation, surface growth and oxidation in the post-processing step so that predicted quantities are at least within an order of magnitude. A total of 20 sections are used. Although the largest PAH species described by the chemical mechanism is benzene [36], steady-state expressions are derived for the formation rate of larger PAHs up to $C_{52}H_{49}$. The computed soot results are found to be relatively independent of the size of the largest PAH