Title: Computed Electronic Structure of Polynuclear Aromatic Hydrocarbon Agglomerates

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Abstract

A technique for linking the physical composition of polynuclear aromatic hydrocarbon (PAH) stacks and clusters to their electronic properties is reported. Kohn-Sham HOMO-LUMO gaps are reported for a series of monomers, stacks, and clusters of six, high-symmetry PAHs (pyrene, coronene, ovalene, circumpyrene, circumcoronene, and circumovalene) generated by DFT calculations with the 6-31G* basis set and a B3YLP exchange correlation functional in NWChem. A previously published, atom-pair minimization algorithm was used to optimize the geometries of the PAH stacks and clusters. HOMO-LUMO gaps decrease with an increase in monomer size; homogeneous stacks and clusters indicate substantial lowering of the HOMO-LUMO gap because of agglomeration effects with the formation of dimers and formation of clusters (two or more stacks) being the most dominant contributions. Heteromolecular particulates had HOMO-LUMO gaps that were strongly influenced by the larger components in the system. The HOMO-LUMO gaps of homogeneous clusters approached a maximum agglomeration effect because of the localization of electronic interactions among adjacent stacks. Previously published, experimentally determined optical band gaps (OBG) from Tauc/Davis-Mott analysis of extinction spectra in various laminar, non-premixed flames had an average OBG of 2.1eV. Based on the computations presented here, this work suggests that clusters with this OBG are comprised of modest molecular size PAH, about the size of ovalene.

Keywords

Soot, polynuclear aromatic hydrocarbons, optical band gap, density functional theory, electronic structure

Introduction

During the combustion of carbonaceous fuels under rich conditions, incomplete combustion will lead to a fraction of the fuel's carbon being rapidly converted into carbonaceous particulate known as soot. The kinetic constraints of this formation process limit the chemical pathways that lead to particle formation. It is well established that initial reaction zone chemistry decomposes the fuel into unsaturated hydrocarbon radicals that undergoes cyclization process to form the first aromatic ring[1]. Hydrogen abstraction followed by successive acetylene addition leads to the formation of polynuclear aromatic hydrocarbons (PAH)[2]. Thermodynamically, this process favors pericondensed systems dominated by six-membered rings[3]. While there are several theories on the mechanism of particle inception from these planar structures[4], it has been our hypothesis that at some point in the chemical growth process the magnitude of the intermolecular interactions will be large

enough for molecules to agglomerate without covalent bonding to form a nascent soot particle. After primary particles are formed, the primary particles will start to aggregate into fractal structures[1, 5].

Soot particle morphology can be thought of as structures on three discrete size scales[6]. Crystallites (referred to in this work as *stacks*) are the basic structural units and are comprised of aromatic structures in turbostratic stacks, with approximately 3-4 PAH in a stack, stabilized by intermolecular interactions[6-11]. The stacks coalesce into roughly spherical primary particles of about 10-30 nm diameter. (Agglomerates of stacks are referred to in this work as *clusters*). Subsequently, these primary particles will aggregate to form soot's fractal structure with a typical size between 200 – 300 nm[6, 12-16].

In our model for nucleation, the transition from chemical to physical growth occurs at modest molecular size (on the order of several hundred atomic mass units) and the electronic properties of soot are dominated by the molecular structure of the PAH that comprise them[8, 17]. This model is complimented by computational efforts from the Violi group, which used molecular dynamics simulations coupled with the metadynamics algorithm to study the effects of molecular size and structure of PAH dimerization. Molecular size was found to play the largest role in dimer stability with the possibility of PAH the size of ovalene dimerizing[18, 19]. A similar onset of agglomeration was reported by the Kraft group at Cambridge, who used their population-balance Polyaromatic Hydrocarbon – Primary Particle model[20, 21] coupled with kinetic Monte Carlo aromatic site algorithm to study the collision efficiency for dimerization. The collision efficiency is related to the diameter and mass of the PAH, and at flame temperatures PAH larger than 360u may dimerize, approximately the size of ovalene [22].

In previous work from our group, soot volume fractions for numerical simulations of a nitrogen-diluted ethylene air non-premixed flame were compared with laser-induced incandescence and Raman spectra of thermophoretically sampled soot[17]. The ratio between the intensity of the “D” peak and the intensity of the “G” peak (I_D/I_G) correlates to the conjugation length of aromatic structures[23] and a conjugation length

between 1.0 and 1.2nm was found in the flames studied[17]. While the I_D/I_G ratio was relatively constant throughout the flame, the soot volume fraction varied with flame location. This supports the hypothesis that PAH agglomeration occurs at a near constant molecular size, but the size and yield of particulate matter depend on the physical growth that follows, initially forming nascent particles and, ultimately, aggregated fractal structures[17, 24].

In an effort to provide additional evidence for this model, our lab has conducted Tauc/Davis-Mott analysis of extinction measurements in a variety of flame systems to determine the optical band gaps of soot particles as function of flame position[8, 25, 26]. The Tauc/Davis-Mott analysis utilizes the near edge of an absorption feature as a probe of the localized states.

$$hv \cdot \alpha \approx (hv - E_g^{opt})^r \quad (\text{Eq 1})$$

where α is the extinction coefficient, E_g^{opt} is the optical band gap (OBG), and r is a constant describing the directness and quantum mechanical allowedness of the optical transition (direct allowed ($r = 1/2$), direct forbidden ($r = 3/2$), indirect allowed ($r = 2$), and indirect forbidden ($r = 3$))[27-29]. The OBG can be determined experimentally when $(hv \cdot \alpha)^{1/r}$ is plotted as a function of photon energy (eV), and the straight line portion of the plot was extrapolated to the x-intercept[28, 30].

Robertson showed that systems with sp^2 character, such as soot, have electronic properties that are dominated by π - π^* interactions and thus the OBG is inversely related to the number of pericondensed aromatic rings in the structure[31-34]. By postulating that the nascent soot particle morphology is dominated by clusters of PAH and that the band gap of these structures could be estimated by the difference between highest occupied and lowest unoccupied molecular orbitals in isolated PAH monomers, the experimentally determined OBG were able to be correlated to molecular size through computations of the electronic structure of series of D_{2h} molecules. The results across all studied flame systems displayed little variation in OBG, and corresponded

to structures with conjugation lengths of about 1nm[8, 25, 26]. While the Tauc/Davis-Mott analysis indicates a characteristic molecular size that is consistent with both computational and experimental results, substantial uncertainties exist linking molecular and electronic structure.

One source of uncertainty is the nature of the transition involved in the band gap. The work of Robertson studying amorphous carbon properties has provided a wealth of information linking the chemical composition, such as hydrogen content and sp^2 versus sp^3 character, with electronic properties[31, 35, 36]. Traditionally, in the Tauc approach, a nondirect transition with the same r value as the indirect transition is used[30, 37]. Using this r value for soot has led to insight into trends regarding structure size, but correlation to molecular sizes results in what many feel is an overestimation of conjugation length[31, 35, 36, 38-41]. In a review article by Robertson, the determination of optical band gaps from extinction measurements is discussed where the arbitrary definition of the band gap in amorphous semi-conductors is emphasized[31]. If the electronic structure of soot particles is dominated by the composite PAH, then the transitions can be treated as direct ($r = \frac{1}{2}$), like those in graphene sheets and ribbons[42-45]. This treatment leads to particle inception sizes that agree with other measurement methods and with computations from several groups[17-19, 22, 25].

A second source of uncertainty in our prior work is that the effect of agglomeration on the electronic properties of PAH has not been considered. The goal of the current study is to analyze the effect of non-bonded interactions of PAH on their electronic and optical properties. Intermolecular potentials[46] for PAH clusters are used to calculate the optimized geometry of dimers, trimers, and clusters of PAH[7]. The electronic structures of these species are then calculated using density functional theory (DFT) providing additional insight into the evolution of the optical band gaps that we have observed in sooting, non-premixed flames.

Methodology

This study focuses on six, high-symmetry (D_{2h} and D_{6h}), pericondensed PAH and their agglomerates: pyrene(py), coronene(co), ovalene(ov), circumpyrene(cp), circumcoronene(cc), and circumovalene(cv). (Structures and properties in the Supplemental Materials). These monomers, with masses from 202– 812u, span a range from small PAH whose dimerization is unlikely at flame temperatures[47], to larger molecules that are expected to play a larger role in particle inception[18, 22].

The starting geometries for the monomers were taken from the Theoretical Spectral Database of Polycyclic Aromatic Hydrocarbons[48]. The geometry for each monomer was further optimized using DFT in NWChem with the 6-31G* basis set and B3YLP exchange correlation functional[49]. Agglomerate geometries were then calculated from these molecules using an atom-pair minimization(APM) algorithm to minimize the binding energy (BE)[7]. Calculations were done for the full suite of homomolecular and heteromolecular dimers. Additional calculations included homomolecular stacks and heteromolecular trimers. To simulate cluster growth, larger clusters were formed using previously-optimized, trimer geometries as the component molecules. The output from the APM reports the BE and generates a NWChem input file.

DFT calculations were undertaken using NWChem v6.5 on George Washington University's high performance computer, Colonial One[49]. For all molecules, the symmetry was set to C_1 and the 6-31G* basis set and a B3YLP exchange correlation functional were used. TD-DFT computations are generally used for excited state energy calculations[26, 48, 50-52]. While this methodology was used in the present study for monomers and dimers, TD-DFT was found to be too computationally expensive for structures larger than approximately 170 carbon atoms. The band gap calculated from the difference in energy between the highest occupied(HOMO) and lowest unoccupied(LUMO) Kohn-Sham(KS) orbitals has been used in previous studies[50-52] and was compared to two sets of TD-DFT calculations: GAMESS calculations using TD-DFT with the 6-31G* basis set and B3YLP exchange correlation functional previously published[26] and TD-DFT computations using Amsterdam

Density Functional software with the DZP basis set with GGA:BLYP functional (available in supplemental material). While the TD-DFT band gap calculations were consistently lower, the trends with increasing molecular size are the same for all three methods. Using the KS band gap has historical precedent [51-53] and allows the study of agglomeration trends of clusters approaching the size of nascent soot particles; a study that was not possible with the more computationally expensive TD-DFT excited state treatment.

Results and Discussion

In this study, homomolecular dimers and trimers, heteromolecular dimers and trimers, and homomolecular clusters were studied to investigate the molecular and agglomeration effects on the electronic structure, specifically the HOMO-LUMO gap. Tabulated data from DFT computations is available in the supplementary material.

Figure 1 compares the HOMO-LUMO gaps calculated for each monomer, as well as the homogenous dimer and trimers at their optimized geometries. The general trend of decreasing HOMO-LUMO gap with increasing monomer size is noticed across all systems. The D_{6h} molecules (coronene and circumcoronene) demonstrate higher HOMO-LUMO gaps than would be expected for a D_{2h} molecule of the same size. It has been suggested that this discrepancy is because of differences in charge transfer because of the high symmetry[52]. In addition to the molecular size effects, the agglomeration from stacking causes an additional decrease in the HOMO-LUMO gap. Over all of the systems studied, dimerization caused an average of 0.44 ± 0.09 eV drop in the gap compared to the monomer, while the dimer to trimer decrease was 0.18 ± 0.04 eV. The increase in the density of states with agglomeration causes the HOMO level to increase in energy, while the LUMO level decreases in energy, decreasing the band gap[52]. Feng et al. studied the effects of molecular size and stacking order on the HOMO-LUMO gaps in stacked PAH systems reporting ranges from 1.0–2.5 eV based on the molecular size, with small changes of 0.3 eV resulting from different numbers of monomers in the stacks and

the stacking order[52]. These results predict smaller agglomeration effects compared to our observations, most likely due to their use of DFT with added dispersion interaction used for both geometry optimization and energy calculations.

Studies of the homomolecular systems isolate agglomeration effects in the HOMO-LUMO analysis, but during soot formation it is unlikely that systems would be molecularly homogeneous. Figure 2 shows the HOMO-LUMO gaps of the complete series of heteromolecular dimers. The standard deviation across the dimer sets decreases with increase in monomer size, which indicates that the dimer electronic structure is dominated by the larger monomer component. In electron density plots of the heterogeneous dimers, it is evident that when there is a large discrepancy between the sizes of the components, the electron density in the HOMO and LUMO energy levels is localized on the larger structure. This results in the HOMO-LUMO gap of the dimer approaching an energy difference similar to that of the monomer of the larger structure. This is illustrated most clearly in the circumovalene series, where the average of the five mixed dimers is 2.04 ± 0.01 eV compared to the circumovalene monomer HOMO-LUMO gap of 2.06 eV. Similar trends are observed in the circumpyrene and ovalene dimers in the instances when they are larger than the other dimer component.

Including two-component, heteromolecular trimers allowed for the investigation of the stacking order on HOMO-LUMO gaps. Two series were studied: one with pyrene and the other with ovalene as the major component; with the other target molecules positioned in either an asymmetric position (AAB configuration) or a centered position (ABA configuration). Across both series and including both configurations, the binding energies of the trimers scaled linearly with the reduced mass of the trimer, agreeing with the literature[7]. When comparing the binding energies of the two trimer configurations, it is evident that when the minority component is smaller than the majority component the BE of system will be higher in ABA configuration than in the AAB configuration. In this ABA scenario, the electron density is localized on the large molecules, which are separated by the smaller molecule. In the AAB configuration the larger molecules are adjacent to each other,

allowing for stronger binding. If the majority component is smaller than the minority component, the ABA configuration produces a smaller binding energy because then the electron density is confined to the center of the structure. Figure 3 depicts this trend with ABA configuration binding energy being larger than the AAB configuration for coronene and ovalene minor components, but the trend inverts for circumcoronene and circumovalene. The HOMO-LUMO gaps are consistently larger for the ABA configuration, while still reflecting the strong influence of the component with largest molecular size.

In addition to the agglomeration and size effects, in systems or subsystems with similar sizes excimer formation is evident as shown by shared electron density between adjacent PAH molecules[54]. For both the KS band gap and TD-DFT band gaps influenced by excimers, charge-transfer effects need to be considered. It is known that standard TD-DFT methods will calculate lower than expected band gaps in these instances which can be somewhat mitigated by use of an asymmetric exchange correlation, such as B3LYP, as done here[55].

In soot, PAH form turbostratic stacks with heights about 0.8–1.2nm and widths of about 1nm[7, 8]. These stacks are generally comprised of 3-4 PAH with a spacing of 0.34nm between stacks[9]. The coalescence of these stacks leads to the formation of primary particles[12-16]. Here, we simulate the effects of continued carbon growth towards the formation of primary particles as clusters of trimers. The small size of pyrene allows for the most complete study of these large agglomerates within our computational limits. Pyrene structures were studied comparing single stacks composed of 2-7 monomers with clusters composed of 2-5 pyrene trimers, with the geometry selected by the APM optimization. The BE scales linearly with number of monomers in the cluster, regardless of whether the configuration is a single stack or multiple stacks. (Although the enthalpic considerations show little preference between a single large stack or several smaller stacks, entropic considerations in a flame would favor several smaller stacks.)

Figure 4 depicts the HOMO and LUMO level electron density plots for the structure comprised of 5 pyrene trimers. This data shows that, at the HOMO and LUMO levels, the electron density is localized on two

molecules, resulting in a density plot analogous to a 2-trimer stack pyrene cluster. Homogenous systems comprised of the same PAH with analogous overlap have similar HOMO-LUMO gaps. This indicates that the agglomeration effects are localized between monomers within a stack or cluster that have electronic orbital overlap and that electron density involved in the HOMO-LUMO gap is not delocalized across the entire stack. Figure 5 depicts the HOMO-LUMO gaps of pyrene, coronene, ovalene, and circumpyrene clusters, starting with the monomer. The pyrene data set also includes both clusters (up to a 5-trimer cluster) and stacks (up to 7 pyrenes). In this system stacks of pyrenes were studied and it was found that in the 6 (and 7) pyrene stacks, the HOMO-LUMO gaps were higher than in the 2-trimer pyrene cluster despite having the same number of pyrene subunits. Similar to the 5-trimer pyrene system, the electron density in the large stacks is confined in such a way that the agglomeration effects have reached their maximum effect.

In the coronene and ovalene series, the dimers formed have a similar configuration for the 2-trimer pyrene cluster, but in the 3-trimer clusters two of the trimers combine to form a hexamer stack. This is consistent with literature where larger PAH form larger stacks[7]. The circumpyrene 2-trimer clusters and 3-trimer clusters, each have a variety of conformations leading to larger ranges in HOMO-LUMO gaps. The clusters in “T” conformation (perpendicular to adjacent stack) tend to correlate to lower HOMO-LUMO gaps, where the structures that are parallel to adjacent stacks lead to larger HOMO-LUMO gaps.

The Boltzmann thermal energy at 1500K is 0.13eV, indicating that variation in HOMO-LUMO gaps within this range is within the thermal excitation distribution. Based on the trends observed in pyrene and the asymptotic behavior observed in all four cluster series, we hypothesize that the dominant agglomeration effects on the HOMO-LUMO gap are in the initial dimerization (with smaller effects for the addition of subsequent layers) and the formation of an adjacent stack. Therefore, by averaging the 2-trimer cluster and larger structures, we can estimate the HOMO-LUMO gap for a homogeneous soot particle: pyrene – 2.67 ± 0.08 eV, coronene – 2.98 ± 0.05 eV, ovalene – 1.88 ± 0.11 eV, and circumpyrene – 1.48 ± 0.20 eV. The difference between the

monomer and cluster HOMO-LUMO gaps across these series was 1.08 ± 0.06 eV. An important observation is that there is no indication that agglomeration effects will cause the HOMO-LUMO gap to decrease to zero (as found in crystalline graphite), but instead will reach an asymptotic minimum based on the molecular size of the component molecules. These findings support the hypothesis that the electronic structure of soot is dominated by the molecular constituents. While only small systems analogous to nascent soot were studied in this work, if this hypothesis holds, the results can be extended to mature soot particles. As computational power expands, our studies will be extended to test this hypothesis.

The goal of this work is to elucidate the effects of molecular size and agglomeration on the electronic structure specifically for the interpretation of spectral properties of nascent soot particles. (In our prior work using Tauc/Davis-Mott analysis to interrogate the size of PAH structures in particle inception, the agglomeration effects were not considered[8, 25].) The results of this computational study indicate that agglomeration effects are significant and should not be ignored, in agreement with a recent publication by Commodo et al. In this work, the authors used cyclic voltammetry, Tauc analysis, and Raman spectroscopy to determine the characteristic monomer size in soot particles.[56] Variations in the conjugation length determined by Tauc analysis were observed, but correlations of the I_D/I_G ratio from the Raman spectra with conjugation length led to consistent results. This discrepancy was attributed to the change in optical properties because of agglomeration effects[56].

On average in laminar non-premixed flames, our Tauc/Davis-Mott analysis found an OBG of approximately 2.1 eV with a variation of about 0.3 eV throughout the flames studied. Based on the computational results presented here, it would suggest that the OBG is consistent with a homogeneous system with monomeric size on the same order as ovalene, compared to the previous correlation that suggested a characteristic size about the size of circumpylene. While homogeneous systems are unlikely in the kinetically controlled particle inception mechanisms, this work and previous studies found that binding energies scale with

reduced mass, meaning molecules are more likely to have significant binding energy if they are on a similar size scale[7]. Additionally, the HOMO-LUMO gap is strongly influenced by the larger molecules in a system, suggesting that spectral properties are also dominated by the larger components of the system. Additional studies of heterogeneous clusters are necessary to better understand the composite effects of binding energy and electronic effects. These calculations would test the hypothesis that maximum agglomeration effects would be observed in systems with similarly-sized PAH components because of optimal electron density overlap. The inclusion of larger heterogeneous systems would allow more realistic modeling of the electronic structure of soot and other nanoscale carbon particles.

Conclusions

A series of monomers, stacks, and clusters of high symmetry polyaromatic hydrocarbons were studied to link the structure of nascent soot particles and their electronic properties to clarify the interpretation of extinction data collected in sooting flame systems. APM was used to optimize agglomerate geometries when building the stacks and clusters. DFT using NWChem[49] with 6-31G* basis set and a B3YLP exchange correlation functional were used to calculate the KS HOMO and LUMO levels. The computations of homomolecular systems were used to isolate the agglomeration effects, where it was found that dimerization ($\Delta\text{HOMO-LUMO} = -0.44 \pm 0.09\text{eV}$) and cluster formation ($\Delta\text{HOMO-LUMO} = -0.47 \pm 0.10\text{eV}$) are the largest contributions. In the study of heteromolecular dimers and trimers, it was found that the larger components in a system strongly influence the HOMO-LUMO gap of the overall structure. In clusters, agglomeration effects are localized to adjacent stacks and HOMO-LUMO gaps approach an asymptote based on the size of the molecules comprising the clusters. Previously published, experimentally determined OBGs from Tauc/Davis-Mott analysis of extinction spectra of a variety of flame systems show an average OBG of 2.1eV. The results of the KS orbital

analysis, binding energies, and prior experimental and computational work suggest nascent soot particles are comprised of modest molecular size PAH, about the size of ovalene [8, 17-19, 22, 25].

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References

- [1] M. Frenklach, *Physical Chemistry Chemical Physics*, 4 (11)(2002) 2028-2037.
- [2] K.O. Johansson, S.A.S. J.Y.W. Lai, D.M. Popolan-Vaida, N.H. K.R. Wilson, H.A.M. A. Violi, *Proceedings of the Combustion Institute*, 35 (In Review)(2014).
- [3] S.E. Stein, A. Fahr, *Journal of Physical Chemistry*, 89 (1985) 3714-3725.
- [4] S.-H. Chung, A. Violi, *Proceedings of the Combustion Institute*, 33 (1)(2011) 693-700.
- [5] H. Richter, J. Howard, *Progress in Energy and Combustion Science*, 26 (4)(2000) 565-608.
- [6] C. Jäger, H. Mutschke, T. Henning, F. Huisken, C. Jäger, H. Mutschke, T. Henning, F. Huisken, *EAS Publications Series*, 46 (2011) 293-304.
- [7] J.D. Herdman, J.H. Miller, *Journal of Physical Chemistry A*, 112 (28)(2008) 6249-6256.
- [8] E.M. Adkins, J.H. Miller, *Phys Chem Chem Phys*, 17 (4)(2015) 2686-2695.
- [9] M. Olzmann, F. Battin-Leclerc, J. Simmie, E. Blurock, (2013).
- [10] A. Sadezky, H. Muckenhuber, H. Grothe, R. Niessner, U. Poeschl, *Carbon*, 43 (8)(2005) 1731-1742.
- [11] M. Rapacioli, F. Calvo, F. Spiegelman, C. Joblin, D.J. Wales, *The Journal of Physical Chemistry A*, 109 (11)(2005) 2487-2497.
- [12] T.C. Bond, S.J. Doherty, D.W. Fahey, P.M. Forster, T. Berntsen, B.J. DeAngelo, M.G. Flanner, S. Ghan, B. Kärcher, D. Koch, S. Kinne, Y. Kondo, P.K. Quinn, M.C. Sarofim, M.G. Schultz, M. Schulz, C. Venkataraman, H. Zhang, S. Zhang, N. Bellouin, S.K. Guttikunda, P.K. Hopke, M.Z. Jacobson, J.W. Kaiser, Z. Klimont, U. Lohmann, J.P. Schwarz, D. Shindell, T. Storelvmo, S.G. Warren, C.S. Zender, *Journal of Geophysical Research: Atmospheres*, 118 (11)(2013) 5380-5552.
- [13] H. Moosmüller, R. Chakrabarty, W. Arnott, *Journal of Quantitative Spectroscopy and Radiative Transfer*, 110 (11)(2009) 844-878.
- [14] P. Buseck, K. Adachi, A. Gelencsér, É. Tompa, M. Pósfai, *Atmospheric Chemistry and Physics Discussions*, 12 (9)(2012) 24821-24846.
- [15] M. Andreae, A. Gelencsér, *Atmospheric Chemistry and Physics*, 6 (10)(2006) 3131-3148.
- [16] D. Lack, H. Moosmüller, G. McMeeking, R. Chakrabarty, D. Baumgardner, *Anal Bioanal Chem*, 406 (1)(2014) 99-122.
- [17] J.D. Herdman, B.C. Connelly, M.D. Smooke, M.B. Long, J.H. Miller, *Carbon*, 49 (15)(2011) 5298-5311.

- [18] J.S. Lowe, J.Y. Lai, P. Elvati, A. Violi, *Proceedings of the Combustion Institute*, 35 (2)(2015) 1827-1832.
- [19] P. Elvati, A. Violi, *Proceedings of the Combustion Institute*, 34 (2013) 1837-1843.
- [20] M. Sander, R.I.A. Patterson, A. Braumann, A. Raj, M. Kraft, *Proceedings of the Combustion Institute*, 33 (1)(2011) 675-683.
- [21] D. Chen, Z. Zainuddin, E. Yapp, J. Akroyd, S. Mosbach, M. Kraft, *Proceedings of the Combustion Institute*, 34 (1)(2013) 1827-1835.
- [22] E.K. Yapp, M. Kraft, *Modelling Soot Formation: Model of Particle Formation*, Springer, 2013.
- [23] M.M. Lucchese, F. Stavale, E.H.M. Ferreira, C. Vilani, M.V.O. Moutinho, R.B. Capaz, C.A. Achete, A. Jorio, *Carbon*, 48 (5)(2010) 1592-1597.
- [24] J.D. Herdman, *The Role of Polynuclear Aromatic Hydrocarbons in Soot Formation: A Theoretical and Experimental Study*, PhD Thesis, George Washington University, Washington, D.C., 2012.
- [25] M. Botero, E.M. Adkins, S.G. Calera, H. Miller, M. Kraft, *Combustion and Flame*, In Publication (2015).
- [26] J.H. Miller, J.D. Herdman, C.D.O. Green, E.M. Webster, *Proceedings of the Combustion Institute*, 34 (2013) 3669-3675.
- [27] J. Tauc, R. Grigorovici, A. Vancu, *physica status solidi (b)*, 15 (2)(1966) 627-637.
- [28] D.L. Wood, J. Tauc, *Physical Review B: Solid State*, [3]5 (8)(1972) 3144-3151.
- [29] E.A. Davis, N.F. Mott, *Electronic Processes in Non-Crystalline Materials*, (2012) 272-301.
- [30] E. Davis, N. Mott, *Philosophical Magazine*, 22 (179)(1970) 0903-0922.
- [31] J. Robertson, *Materials Science and Engineering: R: Reports*, 37 (4)(2002) 129-281.
- [32] L.G. Cancado, K. Takai, T. Enoki, M. Endo, Y.A. Kim, H. Mizusaki, A. Jorio, L.N. Coelho, R. Magalhaes-Paniago, M.A. Pimenta, *Applied Physics Letters*, 88 (2006) 163106-163101-163106-163103.
- [33] A.C. Ferrari, J. Robertson, *Physical Review B: Condensed Matter and Materials Physics*, 61 (20)(2000) 14095-14107.
- [34] A.C. Ferrari, J. Robertson, *Physical Review B*, 64 (2001) 075414-075411-075414-075413.
- [35] C. Casiraghi, A. Ferrari, J. Robertson, *Physical Review B*, 72 (8)(2005) 085401.
- [36] J. Robertson, *World of Carbon*, 1 (Graphite and Precursors)(2001) 249-273.
- [37] J. Tauc, A. Menth, *Journal of Non-Crystalline Solids*, 8 (1972) 569-585.
- [38] J. Robertson, E.P. O'Reilly, *Physical Review B: Condensed Matter and Materials Physics*, 35 (6)(1987) 2946-2957.
- [39] T.C. Bond, *Geophysical Research Letters*, 28 (21)(2001) 4075-4078.
- [40] I. Llamas-Jansa, C. Jäger, H. Mutschke, T. Henning, *Carbon*, 45 (7)(2007) 1542-1557.
- [41] J. Robertson, *Progress in Solid State Chemistry*, 21 (4)(1991) 199-333.
- [42] L. Zhi, K. Müllen, *Journal of Materials Chemistry*, 18 (13)(2008) 1472-1484.
- [43] Y.-W. Son, M.L. Cohen, S.G. Louie, *Physical review letters*, 97 (21)(2006) 216803.
- [44] L. Yang, C.-H. Park, Y.-W. Son, M.L. Cohen, S.G. Louie, *Physical Review Letters*, 99 (18)(2007) 186801.
- [45] G. Gui, J. Li, J. Zhong, *Physical Review B*, 78 (7)(2008) 075435.
- [46] J.H. Miller, W.G. Mallard, K.C. Smyth, *The Journal of Physical Chemistry*, 88 (21)(1984) 4963-4970.
- [47] H. Wang, *Proceedings of the Combustion Institute*, 33 (2011) 41-67.
- [48] G. Mallocci, C. Joblin, G. Mulas, *Chemical Physics*, 332 (2-3)(2007) 353-359.
- [49] M. Valiev, E.J. Bylaska, N. Govind, K. Kowalski, T.P. Straatsma, H.J. Van Dam, D. Wang, J. Nieplocha, E. Apra, T.L. Windus, *Computer Physics Communications*, 181 (9)(2010) 1477-1489.
- [50] G. Mallocci, available at <<http://astrochemistry.ca.astro.it/database/pahs.html>>.
- [51] G. Mallocci, G. Cappellini, G. Mulas, A. Mattoni, *Chemical Physics*, 384 (1)(2011) 19-27.
- [52] C. Feng, C. Lin, W. Fan, R. Zhang, M.A. Van Hove, *The Journal of chemical physics*, 131 (19)(2009) 194702.
- [53] R. Stowasser, R. Hoffmann, *Journal of the American Chemical Society*, 121 (14)(1999) 3414-3420.
- [54] J.H. Miller, *Proceedings of the Combustion Institute*, 30 (1)(2005) 1381-1388.
- [55] A. Dreuw, M. Head-Gordon, *Chemical reviews*, 105 (11)(2005) 4009-4037.

[56] M. Commодо, G. De Falco, A. Bruno, C. Borriello, P. Minutolo, A. D'Anna, *Combustion and Flame*, 162 (10)(2015) 3854-3863.

Figure Captions

Figure 1: HOMO-LUMO gap of monomers(circles), dimers(diamonds), and trimers (triangles) of target molecules.

Figure 2: HOMO-LUMO gap (eV) of heteromolecular dimers. X-axis is the common component in each pair and the bars represent the second dimer component. The deviation in HOMO-LUMO gap across a dimer series is shown by the solid black line (second axis).

Figure 3: HOMO-LUMO gap (eV) of 2-component heteromolecular trimers. Each trimer contains two ovalenes with either ABA(striped bars) or AAB(solid bars) configuration. The lines represent the binding energy of the structures with the dashed line representing ABA and the solid line representing AAB structures.

Figure 4: Electron density plots for the HOMO and LUMO levels of the 5-trimer pyrene structure.

Figure 5: HOMO-LUMO gap(eV) of homomolecular pyrene(squares), coronene(circles), ovalene(x's), and circumpyrene(triangles) structures as a function of number of carbon atoms(symbols). The pyrene data is also fit with an asymptotic equation(dashed line).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5