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Aromatic excimers: evidence for polynuclear aromatic hydrocarbon condensation in flames

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Abstract

A new assignment for the broad band visible laser induced fluorescence observed in rich hydrocarbon flames is offered. It is postulated that emission from aromatic excimers is observed when exciting aromatic aggregates in flames. Because this emission will only occur when the aromatic molecular units are near one another, this assignment would provide evidence for agglomeration of modestly sized polynuclear aromatic hydrocarbons in flames. Both semi-empirical and density functional theory calculations are performed for several small aromatic dimers (benzene, naphthalene, and pyrene). As observed in several prior experimental studies, stacking of the aromatic rings in parallel, overlapping planes leads to excimer transitions. It is suggested that additional near-infrared optical diagnostics in rich flames may provide further support for this theory.
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1. Introduction

Soot formation in hydrocarbon flames is kinetically controlled and occurs in short times (1–10 ms to reach particle diameters of 500 Å) [1]. This constraint of rapid particle formation limits the possible chemical processes that may form soot. Polynuclear aromatic hydrocarbons (PAH) have often been invoked as important intermediates in this chemistry. These species, which are found in all sooting, hydrocarbon flames, have structures similar to the soot's graphic morphology and posses C/H ratios intermediate between most starting fuels (<1) and soot particles (>5). Kinetic mechanisms have been developed for the formation of the first several aromatic rings that

successfully predict measured profiles in reactors, premixed, and non-premixed flames.

At some point in the growth of large species, chemical reaction between two colliding molecules of similar size is no longer a necessary condition for sticking, i.e., the magnitude of the attractive van der Waal potentials will be sufficiently large relative to the kinetic energy of the other molecules in the bath that a aggregate will be formed and will survive. For more than 20 years, researchers in the soot community have studied this problem and several theories have been put forward. In the Twentieth (International) Symposium on Combustion, our group calculated equilibrium concentrations for PAH dimers in flames estimated from monomer concentrations [2]. These dimer concentrations were found to fall short of number densities of the earliest soot particles. Several years later, we revisited the problem from a kinetic perspective.

In this later analysis, the lifetimes of dimers under flame conditions were calculated assuming that either energy of the initial collision could be accommodated by the PAH molecules themselves or could be removed by molecules in the bath. Our conclusion at the time was that this process could occur, but only for relatively large PAH species.

In the 29th symposium, Schuetz and Frenklach [3] used a semi-empirical molecular dynamics approach to calculate dimer lifetimes for pyrene under flame conditions. They found that deposition of energy into internal rotations in the colliding pair greatly extended dimer lifetimes. This result could not have been predicted using our earlier classical calculations that modeled PAH as colliding spheres. Schuetz and Frenklach's finding is an important result because it shifts the onset of PAH condensation to much smaller size ($\approx$300 Da) than that suggested in our calculations ($\approx$600 Da). Further, condensation of four-ring PAH is consistent with particle inception models that transition from chemical to physical growth at this molecular size [4].

Given the important role that PAH aggregates play in the conceptual framework of soot formation theory, no clear experimental evidence has yet been proffered for their existence. In fact, scant data exists for substantial concentrations of PAH larger than pyrene. In this paper, we hypothesize that evidence for PAH agglomerates in flames exists through a reassignment of the broad band laser induced fluorescence that has been observed in soot-producing flames. At the core of this new interpretation of experimental data is the concept of aromatic excimers. In the following pages, we will introduce the literature of aromatic excimers and excitons and review that of broadband laser induced fluorescence experimentation in flames. We will argue that at least some of these fluorescence signals can be attributed to PAH aggregates. Finally, semi-empirical and density functional theory quantum mechanical calculations of electronic transitions for small aromatic aggregates will be provided which lends support to this theory.

1.1. Diagnostics for PAH in flames

Soon after rare gas plasma lasers became available in the 1970s, combustion researchers noted a visible, broadband laser induced fluorescence that was observed in fuel-rich premixed flames or on the rich side of the stoichiometric surface in non-premixed hydrocarbon flames [5–7]. In the ensuing years, scores of papers have been written that report both visible and ultraviolet emissions, and that have attempted to unambiguously assign the fluorescing species [5,8–14]. This rich literature has been reviewed in two recent contributions and will only be summarized briefly below [15,16]. As noted by Smyth et al. [15], there are numerous species that might contribute to an unstructured emission in flames. In general, these candidates must be large enough that their density of states obscures vibrational and rotational band structure, and they must have accessible single photon transitions at the appropriate wavelengths. Polynuclear aromatic hydrocarbon species meet this size criterion, have well known ultraviolet transitions, and combined probe and optical measurements put them in the correct regions of the flames studied.

In general, the wavelength of fluorescence from PAH species increases to longer wavelengths with increasing molecular size [16]. Fluorescence signals have been observed with both ultraviolet and visible excitation. For ultraviolet excitation, two emission maxima can be observed. Although both maxima are attributed to PAH, their profiles are different. In a methane/air non-premixed flames supported on a Wolfhard Parker slot burner, two maxima were observed in the profile of broadband ultraviolet fluorescence when exciting at 282 nm which have slightly different ultraviolet emission spectra [17]. One of these profiles, whose emission maximum occurs $\approx$310 nm, follows a temperature contour with height above the burner surface and closely follows the peak profile for soot particles. The other feature that peaks at $\approx$340 nm follows a convective streamline into cooler, richer flame regions.

In premixed flames UV excitation has been found to excite both a UV and a visible emission depending on flame location and stoichiometry [18–21]. In the recent work of Cajolo et al. [20], the visible emission is only seen with high PAH loading in the flame, but these researchers argue that small aromatic molecules (<4 rings) are unlikely to be its source. Rather, their works suggests that an unidentified constituent of the "condensed species" collected in their flames is responsible for visible fluorescence. Several groups in the soot community have postulated that early particulate matter is composed of aromatic ring systems joined by aliphatic linkages [20,22–24]. Initially, these species might form from reactions between small aromatic radicals and parent compounds or from aromatic radical recombinations. How these molecules would be expected to contribute to visible fluorescence is not fully understood.

In addition to LIF, light scattering using ultraviolet sources has been applied to young particle detection [25,26]. Fractal agglomerate scattering theory suggests that the minimum primary particle size detectable using light scattering is a func-

tion of excitation wavelength and it is likely that primary particles much larger than pyrene-sized PAH would be the source of UV scattering. In a recent paper of Barone et al. [26], AFM images of very small particles sampled from flames are compared with UV light scattering results. In both cases, $D_{6,3}$ was found to be no smaller than 2.5 nm. By comparison, pyrene is less than 1 nm across in its longest dimension.

1.2. Excitons and aromatic excimers

In a laser induced fluorescence experiment for an isolated molecule, an electron is excited by absorption of one or more photons generally from the electronic ground state to an excited state. The electron may return to the ground state by emitting a photon or through one or more non-radiative steps (e.g., quenching.) In a molecular condensed phase, there is a possibility that the excited state might have the electron located on one molecule, and the "hole" on another molecule. Classically, we might view the excited state as columbically bound with the molecule with the additional electron having a net negative charge and the molecule with the hole having a positive charge. The short-lived hole–electron pair is often referred to as an exciton and the bound molecular pair as an excimer.

In the quantum mechanical view, the ground state is a repulsive electronic level (i.e., there is a node in the electron probability distribution between the molecules in a cluster), but the excited state is bound (see Fig. 1).
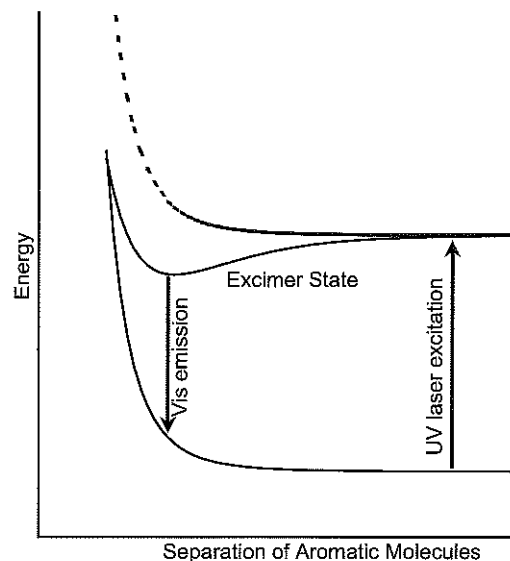

Fig. 1. Potential energy diagram illustrating and contrasting excitonic excitation in isolated molecules and in molecular dimers.

Depending on the molecular pair, bonding may be dominated by charge resonance interaction, exciton (electron–hole) resonance, or mixing of the two [27].

The spectra of aromatic excimers have been studied extensively for several decades in solutions [28–32], adsorbed onto surfaces or in microcrystals [32–37]. The fluorescence from an aromatic excimer is observed substantially red-shifted from that of the isolated molecules, by an amount indicative of the binding energy of the pair. Typical binding energy values for 2–3 ring aromatic excimers range from ≈20–40 kJ/mol. Excimer binding energies are substantially in excess of the magnitude of the van der Waal forces that bind condensed aromatics together [38]. In addition to the shift to lower transition energies, emissions from aromatic excimers are generally broad, featureless, and, in solutions, highly dependent on concentration [39].

2. Computational method

Both classical, semi-empirical, and density functional theory calculations of structures for isolated PAH molecules, dimers, and (in some cases) small aggregates were performed using Hyperchem 7.1 [40] running on a Pentium IV personal computer with Windows XP Professional operating system. In many calculations for PAH systems with less than 5 aromatic rings, molecular structures were first optimized using Molecular Mechanics and refined using the semi-empirical basis set PM3. As noted recently by East and Lim [41], computations of excimer exited state structure (and thus spectroscopy) has not kept pace with the extensive experimental progress due to the fact that inter-chromophore interaction are generally not handled very well in the less computationally expensive semi-empirical techniques. In fact, because the semi-empirical basis sets are not parameterized for these intermolecular electronic interactions, they often predict repulsive interactions for all electronic levels for molecular separations on the order of 3.5 Å (known to be approximate the plane separation distance in most parallel packed aromatic systems) [41]. For more exact predictions of electronic structure, density functional theory calculations were performed for benzene and naphthalene using the 6-31G on the Becke three parameters Lee–Yang–Parr functionals (B3LYP).

Single crystal structures for select larger aromatic systems are available in the Cambridge Structural Database [42]. For larger PAH systems (>4 rings), molecules in the crystal are often arranged in parallel pairs. Depending on the PAH species, the ring systems may substantially overlap

one another (coronene) or barely at all (anthracene) [27]. Pyrene is intermediate between these two extremes with approximately one half of each molecule interacting with the other and a plane spacing of ≈3.53 Å. Perylene and ovalene also exhibit partial eclipse of the aromatic rings for the dimer pair. It has been generally recognized that excimer emission is observed only for ring systems that are partially overlapped as the bound excited state is formed by π–electron interaction between the two rings.

It should be noted that the DFT calculations with Hyperchem are too expensive to allow calculation of pyrene or larger dimer systems. On the other hand, the most stable dimers of aromatic molecules with one or two rings are those with the molecular planes anti-parallel to one another due to quadrupole repulsion between the two ring systems [41]. For illustrative purpose, DFT calculations were performed for both benzene and naphthalene in partially eclipsed, plane parallel geometries. For the larger rings systems, molecular separation was artificially reduced to the point that an attractive excited state could be formed using the semi-empirical technique. It should be noted that both of these artifices are performed for computational expediency, and do not detract form the fundamental and experimentally observed excimer emission phenomenon.

To facilitate calculation of electronic spectra, both semi-empirical PM3 and DFT calculations were run using single excited state configuration interaction within a ±5 orbital manifold. UV/Vis absorption spectra were calculated using the SWizard program [43]. For the latter, it was assumed that all electronic bands were gaussian in shape with a constant 3000 cm^{-1} width.

3. Results and discussion

As noted above, pyrene dimers are thought to occur with the molecules partially eclipsed and

Fig. 3. Contours of electron density in a pyrene dimer from PM3 semi-empirical calculations. Contour surface is drawn at 0.011. (A) Highest occupied molecular orbital (HOMO) illustrating vanishing electron density between rings. (B) Lowest unoccupied molecular orbital (LUMO) showing interaction between p electrons on adjacent rings.
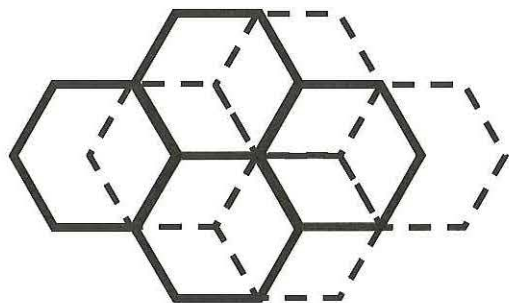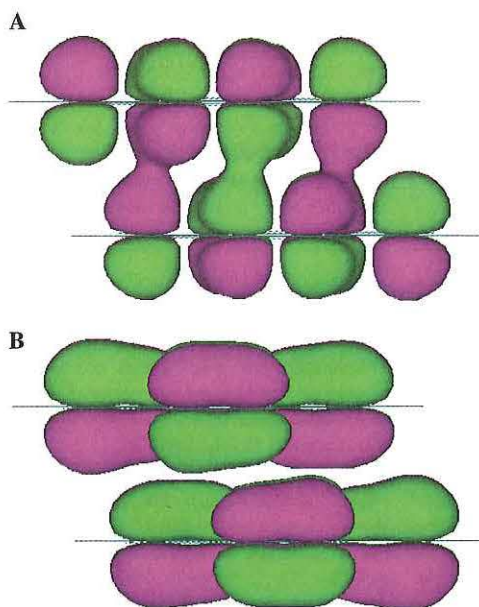

Fig. 2. Overlap of pyrene rings systems in dimers. Molecule closer to viewer is shown in thicker, solid lines for clarity. Coordinate system for Fig. 4 is shown.
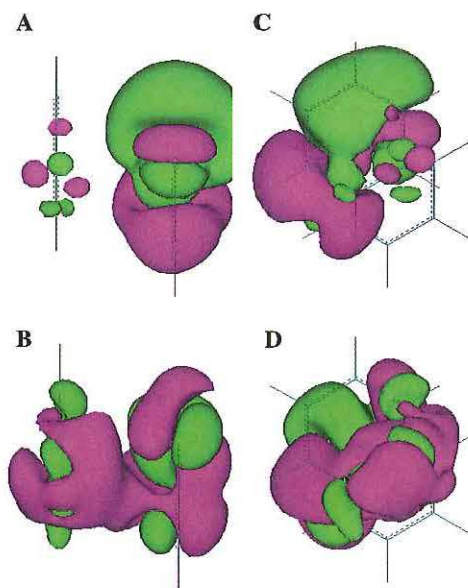

Fig. 4. Contours of electron density in a benzene dimers from DFT calculations. Contour surface is drawn at 0.015. Side views: (A) highest occupied molecular orbital (HOMO) and (B) lowest unoccupied molecular orbital (LUMO). Top views: (C) HOMO and (D) LUMO.
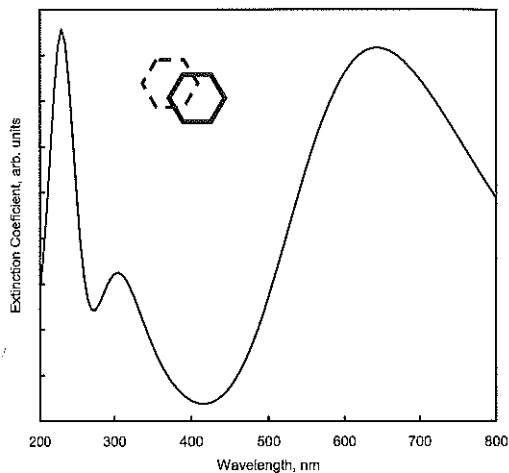
Fig. 5. Predicted electronic transitions benzene parallel dimers from DFT calculations. Dimer orientation is inset.

parallel to one another. Figure 2 shows the orientation for these dimers [27]. Figure 3 shows the result for the semi-empirical calculation of molecular structure for pyrene illustrating the node in electron density between the molecules for the ground state (designated as the highest occupied molecular orbital, or HOMO) and the finite electronic density between the rings in the first excited state (designated as the lowest unoccupied molecular orbital, or LUMO). Although the semi-empirical calculations show electron sharing between the ring systems, they do not predict a visible electronic transition for this
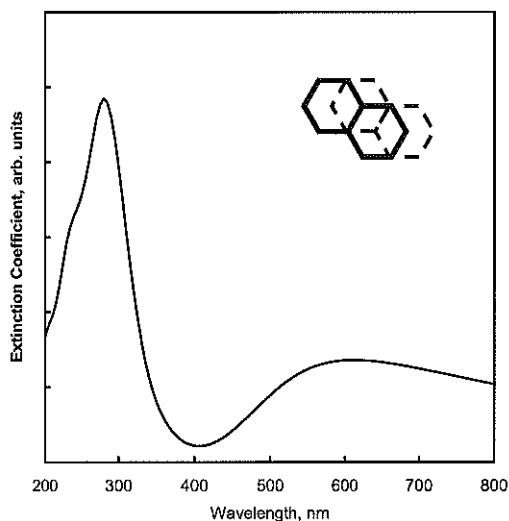

Fig. 6. Predicted electronic transitions naphthalene parallel dimers from DFT calculations. Dimer orientation is inset.

geometry (for the reasons outlined above). As the ring separation is decreased in pyrene, features with finite oscillator strength are observed in the visible.

Figure 4 show the HOMO and LUMO electron density contours for the parallel benzene dimer in the DFT calculations. For these calculations, molecular separation in the dimer was 3.5 Å, typical of aromatic molecular crystals. The orbital map that results from these calculations is extremely dense with transitions to several singlet and triplet levels accessible at energies characteristic of ultraviolet and visible absorption. Figure 5 presents the predicted electronic absorption spectrum for this system. Also shown is the DFT predicted spectrum or benzene monomers.

Similar results were calculated for parallel naphthalene dimers and its predicted absorption spectrum is shown in Fig. 6. These calculations compare favorably with those recently reported by East and Lim [41]. These authors performed DFT calculations for the singlet and triplet electronic states of varying orientations of naphthalene dimer. They found that charge transfer interactions were strongest for naphthalene in the face-to-face geometry and that this stabilization allowed a closer approach for the two monomers. Their work also reports in detail the comparison between DFT electronic state calculations and observed electronic spectra.

3.1. Implications for soot formation

These computational results provide insight to what has been experimentally observed for several decades: small aggregates of modestly sized, polynuclear aromatic hydrocarbons may have visible emissions when excited in the ultraviolet due to the formation of excimer states. Further, these states are bound much more tightly than that which would be expected from aromatic aggregates held together simply by van der Waals interactions.

These results should be considered in the context of what is currently held for the role of PAH in flames, which can be summarized as follows.

First, there is ample evidence for small (1–4 ring) PAH species in flames that temporally precede the observation of particulate matter. However, substantial concentrations of larger PAH have not been observed. Second, kinetic calculations of molecular growth require agglomeration of PAH at modest size (i.e., pyrene) to accurately predict measured particulate profiles. Finally, recent collision dynamic calculations suggest that pyrene dimers may stick together long enough to be collisionally stabilized. If the broadband visible emission observed in rich flames can be attributed

to aromatic excimers, then an important conceptual gap can be closed.

The arguments presented in this paper provide a plausible interpretation of observed experimental data, but like prior assignments for the broadband laser induced fluorescences, do not provide a definitive assignment for the LIF signal. However, these calculations also suggest an additional experimental avenue that, to our knowledge, has not yet been actively pursued. In addition to their visible emissions, some aromatic excimers are known to have transitions that extend into the near-infrared spectral region. Thus, observing and profiling broadband infrared fluorescence in rich flames would complement existing measurements.

4. Conclusions

In this paper, it has been argued that the source of the broadband visible fluorescence observed in rich hydrocarbon flames may be attributed to emission from aromatic excimers. Because this emission will only occur when the aromatic molecular units are near one another, this assignment would provide evidence for agglomeration of modestly sized polynuclear aromatic hydrocarbons in flames. In addition, further optical diagnostics in the near-infrared would provide additional support for this theory.

Acknowledgment

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Comments

Katharina Koshe-Höinghaus, University of Bielefeld, Germany. Your results indicating pairing of small-size aromatics are very suggestive. However, you have not considered ring species with side chains which might have a high reactivity. Could you comment on their potential importance for the fusion process.

Reply. Excimers of PAH dimers have been observed for physically bound dimers of PAH with sidechains [1]. Excimers formed from the reactive condensation of PAH radicals (see text) might also contribute as long as their geometry allows interaction between orbitals on the two aromatic ring systems.

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Hai Wang, University of Southern California, USA. Earlier quantum chemistry calculations showed that the most stable structure of a benzene dimer has one benzene ring perpendicular to the other. Is there a fundamental reason why larger PAH, e.g., dimers/excimers, assume a structure in which the two isometric planes are parallel to each other?

Reply. It has been known for sometime that the benzene dimer *can be* observed as "Tee" shaped. However, recent literature suggests that this is not the only stable configuration [1–4]. For example, Sinnokrot et al. [2] found that the binding energies for three benzene dimer geometries: sandwich, "Tee"-shaped, and parallel-displaced configurations were 1.8, 2.7, and 2.8 kcal mol^{-1}, respectively. It has also been found that benzene-coronene mixed dimers have the rings parallel to one another [5]. The reason that aromatic systems adopt a parallel-displaced geometry may be teased out of the cited references. However, the formation of excimer states is certainly an important factor.

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Christopher J. Pope, USA. A process for PAH condensation is presented that seems more plausible for small PAH than from van der Waals forces. It is reasonable that pyrene, the smallest PAH with an "internal" pair of carbon atoms, would be the first to show such properties.

However, seeing soot formation as starting with pyrene dimerization is an arbitrary construct. PAH do grow beyond pyrene. For assessing the competition between PAH coagulation versus reactions involving σ-radicals, it would help to know the trends in terms of "stickiness" (energies, HOMO–LUMO gap) with respect to PAH size (number of internal carbon atoms) and structure (aspect ratio, 5-membered rings, curvature, substituents). Please comment on any trends you have observed.

Reply. You raise an important point: although in some soot nucleation models pyrene is allowed to physically agglomerate with itself, there is no particular reason that chemistry should stop. As you suggest, physical growth would be expected to increase in irreversibility as binding energy increases (which it certainly does with monomer size.) The calculations I have done so far are too limited in scope to cast much light on this, but they are planned.

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Richard Dobbins, Brown University, USA. Parallel alignment of planar PAH molecules is consistent with the development of Bragg reflections in soot particles resulting in the appearance of "bright domains" in dark field TEM (DFTEM) [1,2]. The formation of bright domains was explained by Oberlin [3] to result from the stacking of planar multi-ring PAHs. Noteworthy is the appearance of faint Bragg reflections in young precursor particles [1,2] which supports the development of the stacked plane configuration described in your paper.

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Reply. Thank you for your comment. It would be interesting to look for other collaborating evidence for the aggregation of modest-sized PAH in flames. Perhaps small angle X-ray scattering might provide additional insight into the structure of these early soot precursors [1,2].

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