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Revealing the molecular structure of soot precursors

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ABSTRACT

The earliest stages of soot formation in flames are believed to involve the formation of small, nanoscale clusters of polycyclic aromatic hydrocarbon molecules. The structure of these clusters is still highly uncertain, however, impeding the construction of quantitative models of soot inception and growth. To provide insight into the structure of incipient soot, we produced nanoclusters of hydrocarbon molecules by annealing coronene films deposited on Pt(111), and examined them with scanning tunneling microscopy. We find that clusters containing ~20–100 molecules, are disordered agglomerations of stacks that are ~5–6 molecules tall. These structures are quite distinct from crystalline coronene, but bear a striking resemblance to recently proposed models for the equilibrium structure of similarly-sized clusters that are assumed to initiate soot formation. In contrast to mature soot, the surfaces of these clusters contain very few molecules with graphitic planes oriented parallel to the surface.

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1. Introduction

Reducing the amount of soot in the environment is desirable for many reasons. For instance, soot particles are believed to adversely affect human health when inhaled [1]. Soot contamination of snow and ice contributes to an average global temperature increase, while the net effect of soot in the atmosphere is potentially large but less well established [2]. Thus, there has been a large number of studies over the past fifty years into the mechanisms of soot formation [3–5]. Of the many processes during soot evolution, starting with chemical reactions between small molecules and ending with the formation of sometimes micrometer-sized soot aggregates, it is the crucial step of particle inception that is perhaps the least understood. One intriguing hypothesis suggests that soot inception is triggered during combustion when planar polycyclic aromatic hydrocarbon (PAH) molecules, each containing 20–30 carbon atoms, begin to condense into small clusters [6]. This initial aggregation process is not well understood, yet it is crucial to predicting when soot forms. The fundamental impediment to progress is familiar to nanoscience: the arrangement of a few molecules assembled into a small particle can be very different

from that in an easier-to-image macroscopic particle [7]. Furthermore, predicting the low-energy configurations of molecule clusters can be exceedingly difficult, especially if they are dominated by long-ranged van der Waals or electrostatic interactions [8]. A promising route to progress is to image the PAH clusters and to compare their structure with theoretical predictions.

Although transmission electron microscopy has been used to characterize the final structure of mature soot in great detail [9], it has not been able to resolve the structures of the 2–5 nm wide clusters involved in soot inception. Atomic force microscopy [10–13] has confirmed the existence of small particles in flames and inspired conjectures of the particles' internal structure [14,15], but has not yet imaged them with molecular resolution.

The crucial question about the clusters' structure is how ordered the molecules are arranged in them. In particular, is there a preferred orientation of the molecules at their surface? This knowledge is critical in understanding how additional molecules are incorporated into the clusters, and thus determines how and when the clusters will evolve into mature soot. In mature soot, the “primary” particles have an onion-like structure in which graphitic layers are oriented nearly parallel to the particle surface. It is unknown if this is also true for incipient soot particles. Recent theories of nanoscale coronene clusters [16] have proposed that the ground state of clusters containing tens of PAH molecules can be very disordered and bear little resemblance to bulk crystalline structures. Because of the large number of degrees of freedom, finding the lowest energy configurations of a few PAH molecules is

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a daunting problem, even when using simplified intermolecular potentials [17]. Further, the nature of the configurations has been found to depend sensitively on the details of the intermolecular potential [18]. This complexity drives the need for experimental data on the molecular structure of these clusters.

Our approach to determining the clusters' structure is to deposit PAH molecules on a surface where atomic resolution scanning tunneling microscopy (STM) can be used to examine how the molecules move and interact as they form clusters. This low temperature surface environment is of course considerably different than the 1000–2000 K gas of dilute PAH molecules in a flame; even so, we will show that this system sheds insight into the ground state structures involved in soot inception.

The adsorption of PAHs has been extensively studied on many surfaces [19]. Most of this past work has focused on the interaction of the PAH molecules with the substrate. For example, determining the strength of their interaction with metal surfaces is important in understanding catalytic reactions of these molecules. In this work, we focus instead on the interaction between the PAH molecules themselves, and on how this affects their aggregation. We chose to study the PAH molecule coronene, $C_{24}H_{12}$, as its size is characteristic of the molecular building blocks of incipient soot [3]. We conducted our experiments on Pt(111) and Cu(111) surfaces. Past work has shown that hydrocarbons interact more strongly with Pt than with Cu [20], so these two substrates were selected to facilitate gauging the impact of substrate interaction on the cluster geometry.

We find that when deposited on Pt(111) at room temperature, coronene initially decomposes to form a “soup” of various PAH molecules similar to what might be encountered in a flame. Molecules deposited on top of this layer form small clusters containing several coronene molecules. We use density functional theory (DFT) to explain the structure and stability of these extremely small clusters. On heating to moderate temperatures, the clusters gradually increase in size, eventually forming complex disordered clusters of 20–100 molecules with a shape similar to those that have been proposed for incipient soot, as discussed in further detail below. Remarkably, very few coronene molecules at the surface of these clusters are oriented parallel to the surface. In contrast, on Cu(111), coronene does not decompose, and instead forms an extremely well ordered monolayer. Diffusion of coronene on top of this ordered layer is so fast that it leads to the immediate formation of macroscopic bulk coronene at room temperature. The structure of the initial clusters could not be observed.

2. Experimental

Our experimental approach is to create 3D clusters of PAH molecules by deposition. 3D clusters are not expected to form at submonolayer coverages because hydrocarbons generally first form a 2D wetting layer on metal surfaces. However, since this monolayer is likely to be the substrate for subsequent cluster formation, it is important to characterize it in detail.

2.1. The molecular wetting layer of coronene on Pt(111)

As described in greater detail in the Methods sections, repeated deposition of coronene via thermal evaporation achieved increasing levels of sub monolayer coverage on the Pt(111) surface, and STM imaging verified the adhesion of the molecule to the surface. Fig. 1a shows sub-monolayer coverage of coronene, in which a hexagonal 2D molecular structure is observed with three ripple-like stripes across it. These stripes are attributed to rows of benzene rings aligned with the close-packed

Fig. 1. (a) STM image of the arrangement of coronene molecules and its fragments on a Pt(111) surface. Sample bias: -0.1 V; Tunnel current: 400 pA. (b) STM image of a saturated molecular layer of coronene molecules on a Cu(111) surface. Sample bias: 1 V; Tunnel current: 100 pA. (A colour version of this figure can be viewed online.)

Pt(111) directions $\langle \bar{1}10 \rangle$, and these features are consistent with other STM investigations of coronene [21–24].

Furthermore, STM revealed that some of the coronene molecules decomposed into fragments, as shown in Fig. 1. Comparison with DFT calculations allowed us to identify these fragments as predominantly triphenylene, pyrene, as well as benzene chains of varying length, similar to naphthalene, anthracene, and tetracene. The apparent heights of these molecules are relatively low (0.15 nm), a result that is consistent with DFT calculations: Fig. 2

Fig. 2. (top) Structure models of the PAH molecules observed in Fig. 1 on Pt(111), along with the STM image simulations (bottom) generated with DFT by determining the contour of constant integrated electronic charge density between the Fermi level and 0.1 eV below. The grayscale spans 0.2 nm. (A colour version of this figure can be viewed online.)

shows DFT image simulations of the PAH molecules on Pt(111) which reproduce the shape and height of the observed features, confirming their identity. Notice that the simulation of the coronene molecule centered on a Pt bridge site reproduces the two-fold (striped) symmetry of the experimental images. Matching the orientation and symmetry of the triphenylene molecule requires centering it on a threefold hollow site. Occasionally, clusters around 0.5 nm in height and 2 nm in width, often resembling graphene patches, were observed scattered about the surface (not shown).

As more coronene is deposited, the surface coverage increases and a higher fraction of coronene molecules remains intact. However, the initially produced fragment molecules appear to prevent the establishment of any long-range ordering on the surface. In instances where coronene molecules neighbor each other, as seen in Fig. 1a, they typically exhibit a set spacing of ~1.1 nm from center to center of neighboring molecules, suggesting a repulsive intermolecular interaction. This distance is consistent with that measured for coronene on graphite and MoS₂ substrates [25]. Similar behavior has been previously observed for both coronene and similar PAH molecules adsorbed on bare metal surfaces such as Ag(100), Ag(111), and Cu(111) [26,27].

To examine how much the presence of the substrate affects the evolution of coronene clusters, we deposited coronene under the same conditions onto Cu(111). As seen in Fig. 1b, the coronene molecules self-assemble into a highly ordered two-dimensional arrangement without any evidence of fragment molecules, consistent with prior literature [18]. We measured the spacing between neighboring molecules to be 1.25 ± 0.1 nm, which is only slightly larger than the spacing on Pt(111). Unfortunately, deposition on top of this layer at room temperature immediately created macroscopic coronene crystals that were visible optically. (Presumably coronene diffusion on top of the ordered coronene substrate is so rapid that small clusters were not formed or decayed too rapidly to be observed.) The subsequent discussion of cluster formation thus focuses on experiments performed on Pt(111).

2.2. Beyond the first molecular layer

It is difficult to deduce the exact coverage of the disordered and inhomogeneous wetting layer. In this paper, we consider the monolayer complete at the inception of a second molecular layer. The structure of the second and further additional layers, which

lack direct contact with the substrate, should be dominated by PAH interactions. How do the molecules arrange themselves under these conditions?

Van der Waals interaction favors molecule stacks that maximize contact area. Typically, PAH molecules can lower the electrostatic repulsion without seriously affecting the van der Waals attraction by a shift or rotation that places the hydrogens of one molecule roughly over ring centers of the other [28], forming “parallel-displaced stack” configurations. However, as explained by Obolensky et al.’s [29] electrostatic ring model, the round shape of the coronene molecule renders such shifts or in-plane rotations much less effective in decreasing the Coulomb repulsion. As a result, T-shaped “edge-to-plane” configurations, which minimize electrostatic repulsion at the cost of giving up some of the van der Waals attraction, could become energetically favorable.

Does such interplay between electrostatic and van der Waals forces affect the coronene multilayers we grow on Pt? Fig. 3 shows the typical morphology of 1.1 ML of coronene. The bright features represent intact coronene molecules residing in the second layer. Apparently, coronene decomposition is deterred, likely due to the “screening protection” provided by the first layer. We propose that most of these bilayer configurations (which appear as protrusions in our STM images) are manifestations of the two structural motifs discussed by Obolensky [29], the parallel-displaced stack and the T-shaped edge-to-plane configuration.

A schematic of the most common bilayer structure (marked by blue arrows in Fig. 3a, referred to here as “doubles”, is depicted in Fig. 3b). Here, two coronene molecules, residing in the second layer, stand upright and are stacked slightly offset from each other in a parallel-displaced manner. (This second-layer dimer thus forms a parallel-displaced stack.) When such a dimer of upright molecules sits on a flat-lying first-layer molecule, the three molecules together form an edge-to-plane motif, with the second-layer dimer contributing the edge and a first-layer molecule the plane.

Another commonly observed structure is the “satellite structure”, marked by orange arrows in Fig. 3a, and shown as a schematic in Fig. 3c: A flat-lying second-layer molecule (the “center”) is surrounded at its perimeter by two to four nearly-upright second-layer molecules (the “satellites”). Here, the center molecule contributes the edge, and the upright satellites the planes. Presumably, the center molecule also participates in a parallel-displaced stack configuration with a first-layer molecule below. The upright satellites presumably also contribute the edge to “T joints” with first-layer molecules below. (The latter two assumptions, which cannot be verified because the buried first-layer molecules are inaccessible to STM, are not crucial for our arguments.)

To test our interpretation of the experimentally observed second-layer features, we relaxed double and satellite configurations in DFT, shown in Fig. 3d and e. Both structures are found to be at least metastable, and DFT reproduces the stack spacing of 0.34 nm in the double and the measured average distance of 1.33 nm between the centers of the satellites (in the satellite configuration), corroborating our structure models depicted in Fig. 3b and c.

Continued deposition revealed that the sticking probability of the coronene decreases with increasing coverage; finally, the coronene surface coverage saturated at approximately 1.3 molecular layers.

2.3. Emergence of soot precursors upon annealing

All of the surface configurations described above are likely to be governed by the limited mobility of PAHs at room temperature. At no time did we observe PAHs move on the Pt(111) surface. In order to make larger clusters further along the path to soot particle

Fig. 3. Second-layer configurations of coronene/Pt(111). (a) STM image of 1.1 molecular layers of coronene on Pt(111). Sample bias: -1 V; tunneling current: 200 pA. Light blue arrows mark examples of the double structure, orange arrows highlight examples of the satellite structure. (b) and (c) Schematics of the doubles and satellites, in which each coronene molecule is represented by a disk. The color scheme, blue for the negatively charged interior and red for positively charged perimeter, has been adopted from Forker et al. [29]. (d) and (e) Top views of double and satellite structure, relaxed with DFT. In the satellite structure, the experimentally observed separation between upright coronene molecules (as denoted with a yellow arrow) is 1.33 ± 0.15 nm, while our DFT calculation predicts 1.4 nm. (A colour version of this figure can be viewed online.)

inception, we gradually enhanced surface mobility by slowly heating the saturated surface.

We heated from room temperature to 430°C in 10° steps before a final 5 minute anneal at 540°C . Slow heating and in situ observation (except for the final anneal) allowed STM to track the structural reformation. This process took place slowly, and there were no abrupt changes in the surface structures until the final

Fig. 4. STM images of coronene/Pt(111) at: a) 70°C , b) 120°C , c) 360°C , and d) room temperature after heating to 540°C ($V = -1$ V, 100 pA, 20×20 nm). Yellow arrows point to molecularly-resolved clusters discussed in the text. (A colour version of this figure can be viewed online.)

anneal. The sequence of STM images of Fig. 4, acquired after annealing to 70°C , 120°C , 360°C , and 540°C , captures the major steps of surface progression: At the lowest temperature of 70°C , shown in Fig. 4a, more coronene molecules had begun to flip up to form the double structure described previously. The first layer also partially dewets supplying the second layer with additional molecules. Satellite structures are more difficult to locate, confirming their relatively low thermodynamic favorability. At 120°C (see Fig. 4b), most double structures have gathered into short chains, which occasionally have side branches or are curled up into compact ~ 2 nm wide knots. Upon raising the temperature to 360°C , the coronene chains have extended and no longer exhibit pairing. Rather, these chains have stacks of coronene similar to first-layer configurations found on Ge(001) [30] which have merged into a continuous network, depicted in Fig. 4c. Neighboring chains often twist around each other, and more instances of larger, tightly packed bundles appear. At this point, all isolated double and satellite structures have vanished.

Finally, at around 540°C , the coronene had bunched up into aggregated three-dimensional super-structures, shown in Fig. 4d. These clusters exhibit a grape-like appearance and are typically 2–3 nm wide. Imaging three-dimensional features with STM is challenging because the surface morphology is convoluted with the shape of the tip, which often obscures important details of the measured surface structure or produces ghost artifacts. This difficulty is compounded by the poor electrical conductance of coronene causing the imaging STM tip to approach the surface more closely to maintain a constant tunneling current, which makes it challenging to avoid destructive tip-sample interactions.

Despite these obstacles, we were able to image some of the 3D clusters with sufficient resolution to make inferences regarding their internal structure. Two examples, marked by arrows in Fig. 4d, are shown at higher magnification in Fig. 5 (a,b). The surface of

Fig. 5. Internal structure of 3D coronene aggregates. a) and b) Detailed STM images of individual 3D coronene aggregates, extracted from the data shown in Fig. 4d c) and d) Estimated internal structure of these aggregates, deduced from the ripples seen in a) and b). In these schematics, each coronene molecule is represented by a blue/pink disk with a diameter of 1 nm. (A colour version of this figure can be viewed online.)

these coronene aggregates is corrugated—it consists of several sets of ~ 1 nm long ridges. The separation between these nearly parallel ridges was measured to range from $3.5 \text{ \AA}$ to $4 \text{ \AA}$. Because of the relatively high concentration of coronene observed on the substrate surface before annealing, we believe that these clusters are composed primarily of coronene molecules. The previously observed fragment molecules are possibly tightly bound to the active platinum surface and thus unable to participate in clustering. By assigning each of the observed nanoridges to an individual coronene molecule, we constructed approximate models for the internal structure of the coronene aggregates. In the model schematics depicted in Fig. 5c and d, each coronene molecule is represented by a blue/pink disk 1 nm in diameter. While these model schematics include only the upper portions of the 3D clusters accessible to the probing STM tip, we assume similar arrangements of molecules to continue into the central and lower portions of the clusters.

Key features of the aggregates' structure are the following. The aggregates are composed of randomly oriented short stacks consisting of up to 5 molecules each. Within each stack, the molecules are nearly parallel, however their orientation can gradually change from molecule to molecule. Within a stack, molecules are slightly shifted laterally, *i.e.* within the plane of the molecule, with respect to their neighbors. These small variations in molecule shift and orientation, consistent with the measured separation between the nanoridges ranging from $3.5 \text{ \AA}$ to $4 \text{ \AA}$, allow the molecule stacks to wrap around each other. Presumably, this flexibility and the variability in stack size facilitates the self-assembly of randomly oriented coronene stacks into 3D aggregates of the observed rather compact overall shape.

All the structural features described above match those of small coronene stacks [12] wrapping around each other as predicted by Totton et al. [17] and Pascazio et al. [18] for nascent soot particles. Experimental examination of the detailed structure of nascent soot generated in flames has not been possible to this date. In order to

obtain microscopy results, the nascent soot particles must be deposited from flame on appropriate substrates. However, because these particles are liquid-like and weak in structure, they will flatten upon impact with the substrate, as AFM results by Barone et al. [10], Abid et al. [11], and Schenk et al. [12,13] reveal. Hence, our experimental data represents the most detailed experimental information to date about the possible internal structure of incipient soot particles.

A notable feature of the coronene clusters observed on Pt is that only a very small fraction of the cluster-surface molecules is oriented parallel to the surface. This is dramatically different from mature soot, where the spherical primary particles have an “onion structure” with almost all benzene rings nearly parallel to the particle surface. This has important implications for the growth of these particles: When an additional coronene molecule collides with such an incipient soot particle, it will not be able to simply stack parallel to an existing coronene molecule. Whether the new molecule is bound strongly enough to irreversibly attach to the particle and grow it will depend on the energy of “T configurations” or require the incipient soot particle to rearrange to accommodate it.

3. Experimental and computational methods

All sample preparation was performed in ultra-high vacuum (UHV) conditions in the low 10^{-10} mbar range. The platinum substrate was prepared through continuous 5 minute cycles of 1500 eV neon sputtering and annealing at 900°C . The copper substrate was prepared via similar means, annealing at 300°C . Thereafter, the bare metal surfaces were kept at room temperature during deposition of coronene through thermal evaporation of the molecule at 120°C using a boron nitride thermal effusion cell. Coronene (sublimed, 99%) was purchased from Sigma Aldrich. For analysis, the sample was transferred to a variable temperature STM (Omicron), without the interruption of vacuum, and imaging was performed under 3×10^{-11} mbar conditions. Low energy electron diffraction and Auger spectroscopy measurements verified the cleanliness and quality of the sample surface. Heating experiments were first performed in the STM stage using the heating element of the sample holder. To anneal to higher temperatures, the sample was then transferred to the chamber manipulator.

DFT calculations were performed using the Vienna Ab-Initio Simulation Package [31]. All of the calculations were on a (6×6) substrate surface unit cell with three atomic layers of metal. Optimizations applied a $2 \times 2 \times 1$ k-point mesh, a 700 eV energy cutoff and structures were relaxed until forces were less than $0.01 \text{ eV/\AA}$. The optimized van der Waals functional optB86b [32] was used. Dipole corrections were taken into account for both the local potentials and total energies. In addition, a vacuum length of at least $15 \text{ \AA}$ separated the slab from cell boundaries perpendicular to the surface.

4. Conclusion

In summary, we have used STM and DFT techniques to characterize the formation of molecular clusters of coronene on Pt(111) and Cu(111) surfaces. On Pt(111), we find that the substrate initially reacts strongly with the coronene molecules, as shown by the decomposition of coronene into fragment molecules. We propose that this interaction is inhibited once a monolayer coverage provides screening protection for subsequent molecular adsorption. At the bilayer, we observed parallel-displaced coronene pairs that assembled into chains, which first grew longer and then wrapped around themselves forming larger clusters as the surface temperature continued to increase. Upon annealing to 540°C , the

coronene molecules transformed into large 3D clusters that bear strong resemblance to proposed incipient soot particles. A notable feature of these particles is that they adopt a structure distinct from large soot particles: rather than having planes parallel to the surface, as in mature soot, they have coronene planes mostly oriented perpendicular to the surface. This has important implications for how additional PAH molecules attach and get incorporated into the growing incipient soot particles. For example, the rate limiting mechanism for the initial stages of soot growth is likely to be a complex cooperative process as the PAH cluster evolves, and unlikely to be governed by a single simple barrier to PAH attachment. The configuration we observe is also likely to be important in soot chemistry – for example soot oxidation rates are believed to be highly sensitive to the surface configuration [33]. While our observations add credibility to the hypothesis that soot inception can occur via aggregation of planar PAHs into nanoclusters, additional experiments would be needed to test alternative mechanisms for the initiation of soot. One hypothesis is that radical sites at the perimeters of PAHs facilitate their growth into large non-planar molecules [4]. It would thus be instructive to perform similar studies with a variety of PAH and aliphatic molecules [5], to assess how the shape and chemistry of the molecules affect their ability to aggregate into nanoclusters. Our success in obtaining molecular resolution of coronene clusters suggests that these experiments are feasible. Future STM experiments might attempt to molecularly resolve the structure of flame generated clusters deposited on substrates [14,15].

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