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Surface reactivity of polycyclic aromatic hydrocarbon clusters

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Abstract

A scheme to characterise surface atoms is proposed to probe molecular representations of homogenous pyrene and coronene clusters. The concept of solvent-excluded surface, which is widely used for proteins, forms the basis of this scheme. The scheme is used to provide insights into the surface reactivity in terms of the surface availability of active atoms and sites for different gaseous species. It was found that the surface availability of active sites varies with gaseous species, system temperature and particle size. The number of active sites available for a small gaseous species is always greater than that for a large species. Surface exposure increases with an increase in temperature and an obvious enhancement exists when transforming to liquid-like configurations. The surface availability decreases with increasing particle size following a linear relation with reciprocal size. The parameter α , which is used in the soot literature to empirically quantify surface reactivity, was further estimated in the context of HACA mechanism and was approximately 0.8–0.9 for reactions between soot particles and acetylene. By exploring one particular pocket on the surface of a coronene cluster with 100 molecules, it was noted that it is feasible for both oxygen and acetylene molecules to penetrate inside the cluster in principle. However, the lifetime of individual pockets was found to be very short compared to the time-scale of a surface reaction, thus ruling out the possibility that surface reactions can take place in regions beyond the boundary by means of surface pockets.

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Keywords: Surface reactivity; PAH; Cluster; Pocket; Alpha

1. Introduction

Surface reactions play an important role in the mass growth of soot, and have been the subject of intense experimental and theoretical investigation [1–6]. However, these investigations are limited by poor understanding of the microscopic structure

of soot. A surface reaction of a soot particle is defined as a reaction between a small gaseous species and an individual active site on the surface of soot particle [7–9]. Usually, the aromatic sites in a particle are not always available for reaction [10–12]. A few reactive sites are “buried” inside the particle structure and not exposed to the gaseous species. This should be necessarily taken into account otherwise it will lead to overestimation of the surface availability of the sites and thus the rate of surface reaction. Experimentally, it is

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extremely difficult to probe this phenomenon because soot particles are structurally heterogeneous [13]. By contrast, Frenklach and Wang [14] proposed an empirical parameter, α , to account the availability of active sites which can react with gaseous species via the HACA mechanism. The main pathway of the HACA mechanism proceeds via the creation of surface radical sites by hydrogen abstraction, and later, the reaction of acetylene molecules with these sites to form 5- or 6-member rings. The growth processes can occur on the free-edge (FE), zig-zag (ZZ) and armchair sites of an individual PAH [15]. Surface oxidation reactions are also initialised by hydrogen abstraction at FE and armchair sites [11,16].

Following Frenklach and Wang's initial investigation, more recent numerical studies have investigated the parameter α and applied it to understand the surface reactions of soot particles in laminar premixed flames [3,16–18] and non-premixed co-flow flames [19,20]. Likewise, a free model parameter known as growth factor g , is included in some population balance models to adjust the rate of surface reaction of PAHs in large soot particles [8,9]. In nature, both parameters α and g represent a steric phenomenon that should be dependent on the microscopic arrangement of a soot particle. However, no one has yet estimated these parameters numerically due to the lack of a satisfactory microscopic representation. Recently, Chen and coworkers studied the thermostability of homogenous pyrene and coronene clusters as analogues for nascent soot particles [21] and demonstrated a phase change due to the addition of mass [22]. These studies provide a representation of these particles that enables the theoretical investigation of their surface reactivity.

To enable the probing of a surface representation, Richards [23] first described a solvent-accessible surface (SAS) as the surface was traced out by the center of a spherical probe representing a solvent molecule of a defined size using a “rolling

ball” algorithm [23] (see the dashed black line on Fig. 1). Later, a more appropriate concept, the solvent-excluded surface (SES), was proposed to represent the actual surface of a configuration [24] (see the orange solid line on Fig. 1). This surface contains the parts of the van der Waals surface of the atoms that are “touched” by the probe and linked by a series of concave and saddle-shaped surfaces between the atoms. In practice, the SES can be computed using a “rolling ball” algorithm [25–27]. Using the SES representation, reactive regions known as “pockets” can be identified inside a configuration [28]. Technically, a pocket inside a configuration is defined as an empty concavity on the surface of the configuration into which bulk gaseous or solvent atoms can gain access [29,30]. In other words, a pocket represents a mouth-type opening connecting the interior with the outside atmosphere or solution. Obviously, pocket detection can geometrically characterise the surface porosity of a target configuration and thus we can investigate whether gaseous or solvent atoms can penetrate inside a configuration and react with the active sites via individual pockets.

In this work, the surface properties of homogenous pyrene and coronene clusters, including the surface availabilities of hydrogen atoms, FE and ZZ sites, are investigated microscopically using geometric analysis. For the first time, we can examine the surface reactivity of small PAH clusters directly from their molecular arrangements. We study the dependence of the surface availability on the gaseous species, system temperature and molecular size. We also identify surface pockets located on a particular particle and investigate whether gas-phase species can access regions beyond the boundary of the configuration of a coronene cluster via individual pockets.

2. Computational method

2.1. Molecular cluster

The current work investigates the surface reactivities of a number of clusters, P_N . N denotes the number of molecules and varies from 50 to 500. P represents either pyrene or coronene. All the clusters were taken from previous work [21] in which the detailed microscopic representations were assembled and equilibrated using conventional Molecular Dynamics (MD). For each size, 100 different configurations have been extracted from a trajectory of 1 ns which is considered to represent an equilibrium state. The reported surface properties are computed by averaging over these configurations and the standard deviations are used to build the error bars.

The main concerns of this work are the surface availabilities of hydrogen atoms, FE and ZZ sites

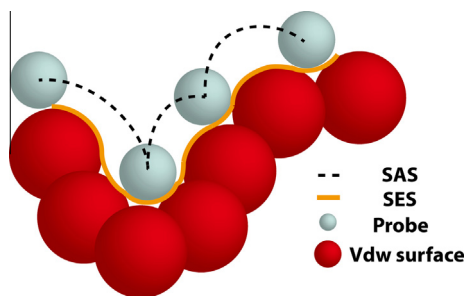


Fig. 1. Illustration of the “rolling ball” algorithm and the definition of the solvent accessible surface (SAS), the solvent-excluded surface (SES), and the van der Waals (Vdw) surface.

which determine the rates of surface reactions. There are 6 FE and 4 ZZ sites on a pyrene molecule, and 6 FE and 6 ZZ sites on a coronene molecule [31]. To identify the site types on the surface of microscopic representations, an index is assigned to each atom of the constituent pyrene and coronene molecules, such that the site type can be determined by analysing the atom indices.

2.2. Molecular surface analysis

SES was used to describe the molecular surface of the configurations in this work because it provides a more accurate description of the actual surface compared to that of SAS. The SES area was determined by the MSMS 6.2.1 program [32] which computes the surface area using a “rolling ball” algorithm. The radii of the carbon and hydrogen atoms are taken from their standard van der Waals radii as 1.7 and 1.2 Å, respectively [33]. Figure 2(a) shows a configuration approximated by SES using a spherical probe, whilst Fig. 2(b) illustrates the approximation of a configuration by representing atoms with solid spheres. Clearly, SES connects all the surface atoms and forms an irregular molecular surface.

The contributions of each atom on the SES area can be calculated, and any atom with non-zero contribution is interpreted as a surface atom. The site information is obtained by analysing the indices of the surface carbon atoms. This characterisation of the surface atoms builds the basis of this work. The scheme incurs negligible computational cost - a few seconds per configuration - and is highly extensible to future work because only the structure of a particle is required as input.

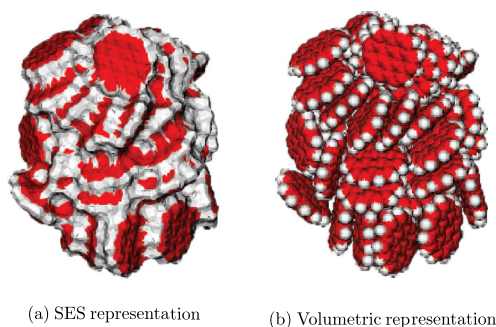


Fig. 2. Solvent-excluded surface (SES) and volumetric representation of a liquid-like coronene₅₀ cluster at 500 K. The red color represents the carbon atoms whilst the white color represents the hydrogen atoms. The solvent-excluded surface representation in Fig. 2(a) is generated using a probe with 0.17 nm radius, which is analogous to the size of a single carbon atom. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Note that the characterisation is instantaneous and evolves in time as the molecules rearrange.

To enable the analysis of a target configuration, the surface availability of atom or site i , i_{surf} , is introduced to represent the availability of the active atom or site on a molecular surface and it is computed by

$$i_{\text{surf}} = \frac{S_i}{N_i}, \quad \text{where } i \in \{\text{hydrogen atom, FE and ZZ sites}\}. \quad (1)$$

S_i is the number of atoms or sites of type i accessible to a specific probe and N_i is the total number of atoms or sites of type i within the configuration. The physical representation of i_{surf} is the accessibility of atoms or sites of type i on the particle surface to the gas-phase species used as the probe. Thus, the surface accessibility to different gas-phase species can be estimated using a probe with a size corresponding to the size of a specific gas-phase molecule. This work considers four different-sized probes (Table 1) to represent the major gaseous species involving in the surface reactions of soot particles. As both oxygen and acetylene molecules are symmetrically linear molecules, the size of the oxygen and acetylene molecule is taken from half of their structures or one single oxygen atom and one C–H fragment, respectively.

2.3. Pocket detection

Surface pockets always act as pathways for gaseous molecules to gain access to the interior of a particle and represent the surface porosity of one particular particle. In this work, we used the pocket detection software package *Fpocket* [30], to identify pockets on the surface of homogeneous PAH clusters and probe the corresponding surface porosity. This package was previously used in the characterisation of protein binding sites for ligand design [34] and it has been introduced in detail elsewhere [30]. Technically speaking, *Fpocket* performs a pure geometric analysis of the target configuration using the concept of

Table 1
Van der Waals radii for different gaseous species.

Probe	Radius (Å)
Hydrogen atom	1.2
Oxygen molecule ^a	1.52
Carbon atom	1.7
Acetylene molecule ^b	2.0

^a The size of the oxygen molecule is taken from the size of a single oxygen atom or half of its structure.

^b The size of the acetylene molecule is taken from the length of a C–H fragment or half of its structure.

alpha spheres (Fig. 3), introduced by Liang et al. [29]. By definition, an alpha sphere is an empty spherical region that is bounded by the centres of four atoms within the cluster. By scanning the target configuration, an ensemble of different-sized alpha spheres can be identified, and an ensemble of pockets are identified from overlapping sets of alpha spheres. Note that it is necessary to impose upper and lower bounds on the allowed size of the alpha spheres. This is required to prevent the identification of large alpha spheres along the surface of the configuration and small alpha spheres throughout the configuration.

In this work, both carbon and hydrogen atoms were considered to bound the alpha spheres, whilst hydrogen atoms are usually ignored when investigating the surface of a protein [30]. The maximum allowed radius of the alpha spheres was 5 Å while the minimum radius was computed as the sum of the specific probe size and the radius of carbon which is 1.7 Å. Since the implementation of *Fpocket* does not account for the size of atoms, one has to add the size of atoms to the minimum radius to overcome this issue. For example, the minimum radius was 3.7 Å when using an acetylene molecule as the probe (Table 1). Such pockets are capable of accommodating at least one acetylene molecule and acting as a pathway allowing acetylene molecules physically to “touch” the interior of a configuration.

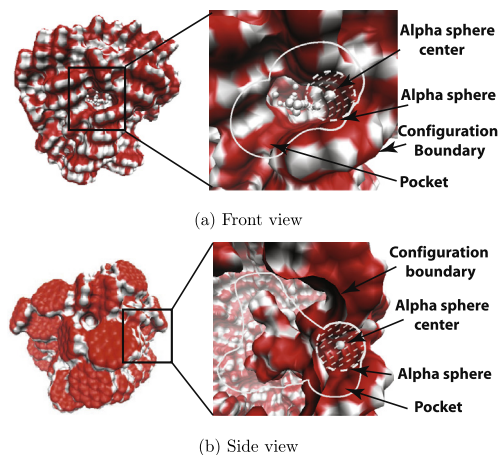


Fig. 3. Illustrations of alpha spheres on a liquid-like coronene₁₀₀ cluster at 500 K using a probe with 0.12 nm radius. The solid white small spheres represent the alpha sphere centers, and one of alpha spheres is highlighted by the dashed lines. The solid white line outlines a pocket which is built by a set of the alpha spheres using *Fpocket* [30]. The boundary of the configuration is highlighted to distinguish the inside of the configuration from the outside environment.

3. Results

3.1. Probe dependence of the surface availability

Figure 4 shows the surface availabilities of hydrogen atoms, FE and ZZ sites as a function of probe size. The surface availabilities decrease with increasing probe size. When the size of probe is less than 0.6 Å, the reported surface availabilities approach unity. However, as no species have such a small size (Table 1), this suggests that no molecule can move unrestricted within the configuration. When increasing the probe size, the reported surface availabilities asymptote as probes cease to pick out the detail between adjacent atoms, but instead pick out the atoms and sites that are accessible at the boundary of the configuration.

3.2. Temperature dependence of the surface availability

The surface availability of hydrogen atoms on coronene₅₀ and coronene₅₀₀ clusters have been examined to illustrate the impact of temperature (Fig. 5). The results are reported in terms of the reduced temperature T_r , defined as $T_r = T_{\text{actual}}/T_{\text{melting point}}$. The melting points of individual clusters were taken from previous work [21]. The maximum reduced temperature in this work was 1.13 or $T_{\text{actual}} = 650$ K for a coronene₅₀₀ cluster [21]. At higher temperatures these particles are highly mobile and favour thermal dissociation for $T_r \geq 1.1$ [35]. We emphasise that, while the absolute temperatures considered here may be significantly lower than typical flame temperatures,

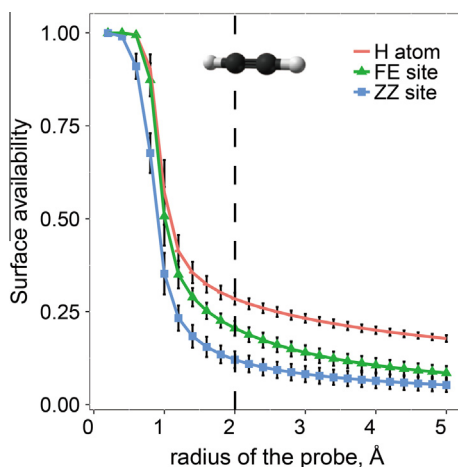


Fig. 4. Surface availabilities of hydrogen atoms, FE and ZZ sites of a liquid-like coronene₅₀₀ cluster at 575 K as a function of the probe size. The error bars are the standard deviations computed from 100 different samples of the configuration. The size of an acetylene molecule is highlighted by the dashed line.

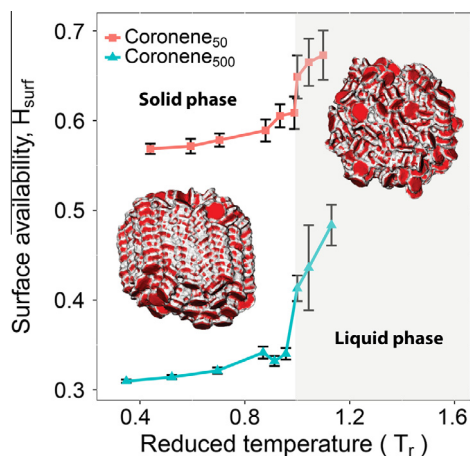


Fig. 5. Surface availability of hydrogen atoms on coronene₅₀ and coronene₅₀₀ clusters as a function of the reduced temperature. The radius of probe is 1.2 Å which is analogous to that of a hydrogen atom. The configurations of the coronene₅₀₀ cluster at $T_r = 0.96$ (left) and 1.0 (right) are also embedded on the plot. The melting point of both coronene₅₀ and coronene₅₀₀ are taken from Chen et al. [21] and are 455 and 575 K respectively. The error bars are the standard deviations computed from 100 different samples of the configuration.

the qualitative argument presented here involves only *reduced* temperatures and thus remains valid at flame conditions (by similarity, using larger PAHs and/or clusters).

Figure 5 shows that the particles at higher temperatures yield higher surface availabilities, and that there is a pronounced increase in the surface availability as the particles melt. Similar observations are found for both FE and ZZ sites. Not surprisingly, the increase in surface availability as the particles melt is accompanied by a significant change in the particle morphology. Previous work [21] has demonstrated that the solid particles are composed of multiple parallel stacks of PAHs with clear surface edges, whilst the melted particles are composed of small stacks of three to seven PAHs and exhibit very irregular surfaces. The ordered crystal-like morphology of the solid particles limit the access of gaseous species and consequently, the number of surface hydrogen, FE and ZZ sites is limited. By contrast, the irregular surface of the melted particles allows a higher exposure to gaseous species and enhances the surface availabilities of hydrogen atoms, FE and ZZ sites. However, this observation disagrees with common estimates of the parameter α , which accounts for the availability of reactive sites on particle surface and it is believed to decrease with temperature [14,16,18]. This is due to differing assumptions made about the quantities. In references [14,16,18], α was assumed to be a global property of the particle distribution whilst in this work, the

surface availability, i_{surf} is treated to be a local property which varies from particle to particle.

3.3. Particle size dependence of the surface availability

In a recent expression of the parameter α [16], the parameter is not only temperature dependent, but also particle size dependent. Similarly, Fig. 6 shows the surface reactivities of different-sized pyrene and coronene clusters at their melting points using a probe representing an acetylene molecule. It is found that the surface availability reduces with increasing particle size, and follows a linear relation with reciprocal size. The surface availability of the coronene clusters is approximately 0.05–0.1 higher than that of the pyrene clusters. From the slope of the fitted lines, we can extract information about the decay rates of these surface properties. The decay rate of the FE and ZZ sites is approximately 0.75 and 0.45 times of that of hydrogen atoms. The lower availability of ZZ versus FE sites is attributed to the concave structure of the ZZ sites, where the carbon atom at the centre of the concave region is expected to be less accessible than the equivalent atom in a FE site.

On Fig. 6, the surface availabilities of hydrogen atoms, FE and ZZ sites lie in the ranges 0.2–0.6, 0.2–0.4 and 0.1–0.3, respectively for nascent soot, interpreted as particles less than 10 nm in diameter. The surface availabilities are significantly lower (and well below 0.1) for mature soot, interpreted as particles greater than 50 nm. Following Frenklach's definition of the parameter α [14], α corresponds to the proportion of sites on a particle surface which are accessible by gaseous species. From Fig. 8, we can approximate α by considering that the pocket surface is inaccessible due to its short lifetime and accordingly, α for acetylene-driven processes is about 0.8–0.9. Such approximation can be interpreted as an upper bound for α because other mechanism may contribute as well. This offers a rationale to guide the selection of the parameter α in flame modelling. For instance, the value of α from a set of laminar premixed flames [36] is always greater than 0.4 for the flames studied by Appel et al. [16]. More recently, Dworkin et al. [37] optimised the parameter α by fitting the predicted maximum soot volume fraction to experimental data for a co-flow ethylene/air non-premixed flame. It was found that the experimental trends of the soot fraction were successfully captured using a constant α as small as 0.078. Saffaripour et al. [20] further proposed an alpha value of 0.0045 to improve the quality of their model. Compared with findings in this work, all of the above values lie below the suggested upper bound of parameter α . Blanquart and Pitsch [12] found that the surface reactivity of small spherical particles remains around 1×10^{19} sites/m² whilst it can reach up to 7×10^{19}

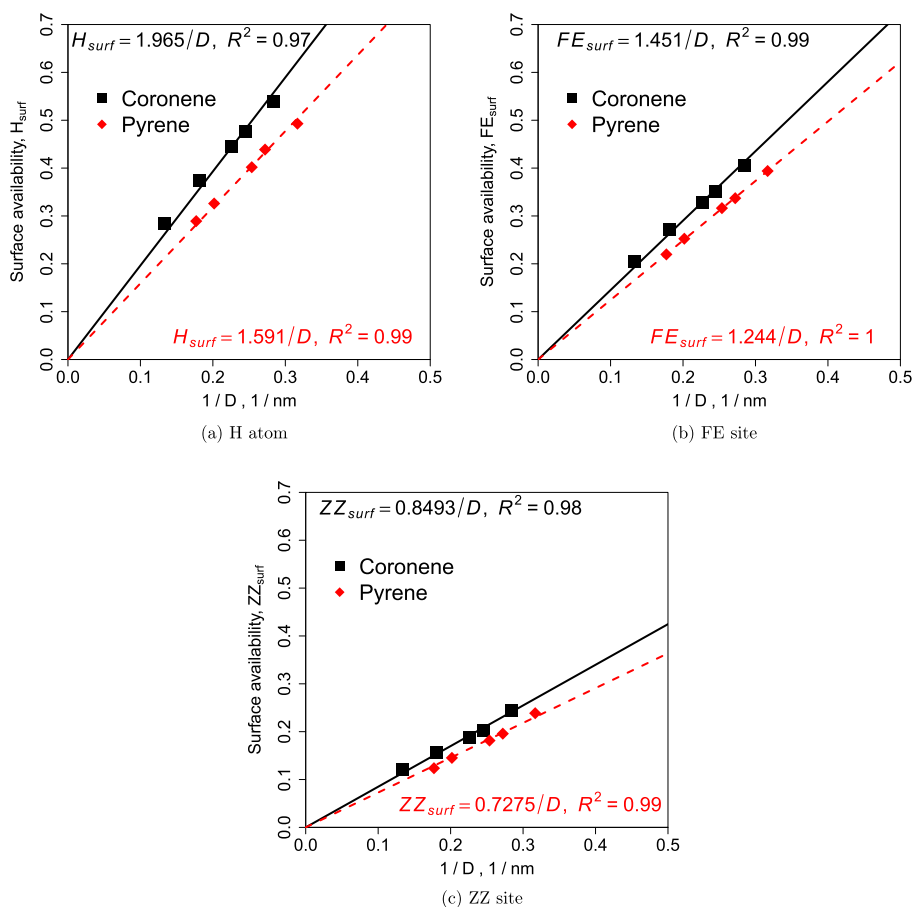


Fig. 6. Surface availabilities of hydrogen atoms, FE and ZZ sites on pyrene and coronene clusters at $T_r = 1.0$ as a function of the reciprocal of particle diameter. The probe radius is 2.0 Å which is analogous to that of an acetylene molecule. The equation of the straight lines of best fit and the corresponding R_2 value are shown at the top of each plot for the coronene and the bottom of each plot for the pyrene.

sites/ m^2 for large aggregates. To compare with these values, we have to recast the surface availability with reference to an equivalent sphere (see Table S2 in Supplemental Material). For small particles, the value fits with our estimation very well. In this work, we estimated that the surface reactivity reduces with the increase of the particle size, but by contrast, Blanquart and Pitsch [12] proposed otherwise. Specifically, the surface reactivity of large particles was overestimated by roughly one order of magnitude. In summary, the upper bound of the parameter α for acetylene-dominated processes can be used to guide the fidelity of predictions from numerical simulations where the surface processes dominate the mass growth of soot.

3.4. Surface pockets

To investigate explicitly the surface pockets, one particular pocket on a coronene₁₀₀ cluster at

500 K was carefully examined using different probe sizes ranging from 1.2 to 2.0 Å (Fig. 7). The existence of pockets in the coronene₁₀₀ clusters supports the proposition that it is feasible for small gaseous molecules to penetrate inside a particle. As outlined by the white solid line, the size of the pocket decreases with the increase in the probe size. This supports the observation that a small probe gains a larger accessibility within a configuration, whilst the accessibility that of a large probe is limited. It is also noted that the depth of the pockets vary with the size of the probe. The depths of the pockets in Fig. 7 are approximately 1.5 nm (Fig. 7a), 1.1 nm (Fig. 7b) and 0.4 nm (Fig. 7c). Compared to the average 0.35 nm layer separation of a PAH stack [38], this pocket provides a pathway for an oxygen molecule to access PAHs located up to 3 layers deep within a PAH stack on the surface whilst even an acetylene molecule can access at least 2 layers deep.

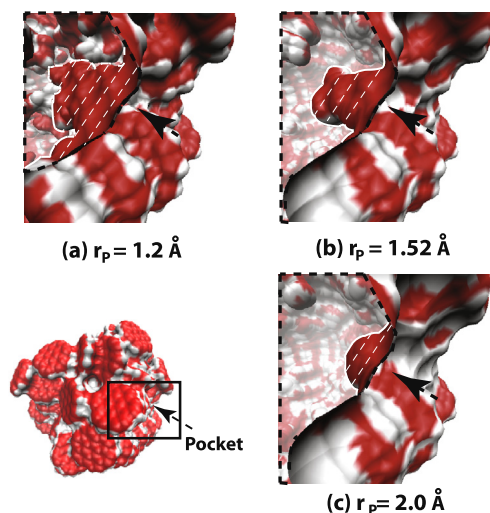


Fig. 7. Side view snapshots of a pocket on a liquid-like coronene₁₀₀ cluster using a probe of radius $r_p = 1.2$ Å (a), 1.52 Å (b) and 2.0 Å (c) at 500 K. The red color represents the contribution of the carbon atoms, whilst the white color represents the contribution of the hydrogen atoms to the SES. The black arrows point to the location of the pocket on the configuration. The black dash lines highlight the sections of the configuration. The white solid lines outline boundary of the surface pockets. The dashed white lines fill the extent of the pockets beyond the boundary of the configuration. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

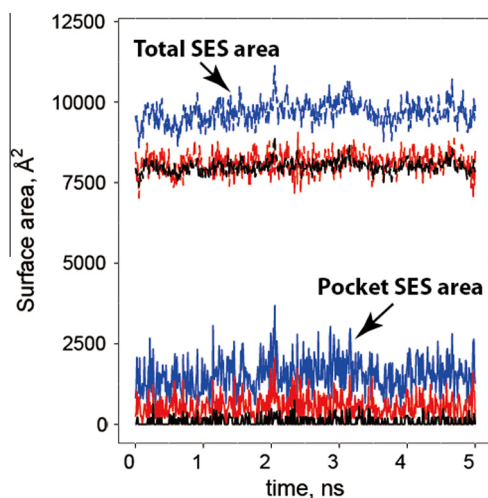


Fig. 8. Evolution of pocket SES area and total SES area of a liquid-like coronene₁₀₀ cluster at $T_r = 1.0$ (500 K) using a probe of radius $r_p = 1.2$ Å (blue), 1.52 Å (red) and 2.0 Å (black). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

We further examined the lifetime of pockets on a particle to investigate whether gaseous molecules can access regions beyond the boundary of a particle via pocket. Figure 8 shows the transient evolution of the pocket and total SES area of the coronene₁₀₀ clusters. Both the pocket SES area and the total SES area fluctuate around an average value. The fluctuations are caused by molecular rearrangements and indicate that individual pockets have a short lifetime and continuously appear and disappear. The lifetime of an individual pocket on a liquid-like particle is typically in the order of 10 ps as the molecules within this cluster have a very high mobility [21]. By contrast, the time scale of a surface reaction is in the order of 1 μ s [9]. The large time scale difference suggests that surface reaction are unlikely to occur beyond the actual boundary of a configuration via pocket due to the short lifetime of a pocket.

4. Conclusion

We propose a scheme to characterise surface atoms based on the solvent-excluded surface and demonstrate how to extract the surface properties from a molecular arrangement using this scheme. The availabilities of the surface active atoms and sites including hydrogen atoms, FE and ZZ sites are investigated to shed a light on the surface reactivity of homogenous pyrene and coronene clusters with diameters from about 3 to 8 nm. The accessibility of the active sites on the clusters vary with gas-phase species. Small species usually have a high accessibility while the accessibility of large species is limited. The surface availability also shows a temperature and particle size dependence. Higher temperatures lead to a higher exposure of the molecular surface. Furthermore, the surface availability is significantly enhanced when crossing the melting point because of the change in the particle morphology. The parameter α for acetylene-based processes is estimated by considering that the pocket surface is inaccessible to gaseous species due to its short lifetime. By exploring one particular pocket on the surface of a coronene₁₀₀ cluster with different probe sizes, it is found that both oxygen and acetylene molecules are able to access certain regions beyond the boundary of a particle in principle. It is also noted that the lifetime of pockets is very short compared to the time scale of a surface reaction, and this fact precludes the possibility that gas-phase species can react with active sites buried inside a configuration.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.proci.2014.06.140>.

References

- [1] M. Balthasar, F. Mauss, A. Knobel, M. Kraft, *Combust. Flame* 128 (2002) 395–409.
- [2] R.I.A. Patterson, J. Singh, M. Balthasar, M. Kraft, W. Wagner, *Combust. Flame* 145 (2006) 638–642.
- [3] A. Kazakov, H. Wang, M. Frenklach, *Combust. Flame* 100 (1995) 111–120.
- [4] C. Kim, A. El-Leathy, F. Xu, G. Faeth, *Combust. Flame* 136 (2004) 191–207.
- [5] A. Raj, M. Celnik, R. Shirley, et al., *Combust. Flame* 156 (2009) 896–913.
- [6] A. D'Anna, J.H. Kent, *Combust. Flame* 152 (2008) 573–587.
- [7] K. Leung, R. Lindstedt, W. Jones, *Combust. Flame* 87 (1991) 289–305.
- [8] M. Sander, R.I. Patterson, A. Braumann, A. Raj, M. Kraft, *Proc. Combust. Inst.* 33 (2011) 675–683.
- [9] D. Chen, Z. Zainuddin, E. Yapp, J. Akroyd, S. Mosbach, M. Kraft, *Proc. Combust. Inst.* 34 (2013) 1827–1835.
- [10] J. Bhatt, R. Lindstedt, *Proc. Combust. Inst.* 32 (2009) 713–720.
- [11] M.S. Celnik, M. Sander, A. Raj, R.H. West, M. Kraft, *Proc. Combust. Inst.* 32 (2009) 639–646.
- [12] G. Blanquart, H. Pitsch, *Combust. Flame* 156 (2009) 1614–1626.
- [13] M. Schenk, S. Lieb, H. Vieker, et al., *Chem. Phys. Phys. Chem.* 14 (2013) 3248–3254.
- [14] M. Frenklach, H. Wang, *Symp. (Int.) Combust.* 23 (1991) 1559–1566.
- [15] A. Raj, P.L. Man, T.S. Totton, M. Sander, R.A. Shirley, M. Kraft, *Carbon* 48 (2010) 319–332.
- [16] J. Appel, H. Bockhorn, M. Frenklach, *Combust. Flame* 121 (2000) 122–136.
- [17] F. Xu, P. Sunderland, G. Faeth, *Combust. Flame* 108 (1997) 471–493.
- [18] F. Xu, K.C. Lin, G.M. Faeth, *Combust. Flame* 115 (1998) 195–209.
- [19] M. Kholghy, M. Saffaripour, C. Yip, M.J. Thomson, *Combust. Flame* 160 (2013) 2119–2130.
- [20] M. Saffaripour, M. Kholghy, S. Dworkin, M. Thomson, *Proc. Combust. Inst.* 34 (2013) 1057–1065.
- [21] D. Chen, T.S. Totton, J.W. Akroyd, S. Mosbach, M. Kraft, *Carbon* 67 (2014) 79–91.
- [22] D. Chen, T. Totton, J. Akroyd, S. Mosbach, M. Kraft, *Carbon*, in press (2014b). <http://dx.doi.org/10.1016/j.carbon.2014.04.089>.
- [23] B. Lee, F. Richards, *J. Mole. Biol.* 55 (1971) 379–400.
- [24] M. Connolly, *Science* 221 (1983) 709–713.
- [25] F.M. Richards, *Ann. Rev. Biophys. Bioeng.* 6 (1977) 151–176.
- [26] M. Connolly, *J. Appl. Crystallogr.* 16 (1983) 548–558.
- [27] T.J. Richmond, *J. Mole. Biol.* 178 (1984) 63–89.
- [28] B.K. Shoichet, I.D. Kuntz, D.L. Bodian, *J. Comput. Chem.* 13 (1992) 380–397.
- [29] J. Liang, C. Woodward, H. Edelsbrunner, *Protein Sci.* 7 (1998) 1884–1897.
- [30] L.G. Vincent, S. Peter, T. Pierre, *BMC Bioinf.* 10 (2009) 106.
- [31] M.S. Celnik, A. Raj, R.H. West, R.I.A. Patterson, M. Kraft, *Combust. Flame* 155 (2008) 161–180.
- [32] M.F. Sanner, A.J. Olson, J.C. Spehner, *Biopolymers* 38 (1996) 305–320.
- [33] A. Bondi, *J. Phys. Chem.* 68 (1964) 441–451.
- [34] S. Henrich, O.M.H. Salo-Ahen, B. Huang, F.F. Rippmann, G. Cruciani, R.C. Wade, *J. Mol. Recognit.* 23 (2010) 209–219.
- [35] M. Schmidt, A. Masson, C. Bréchnignac, *Int. J. Mass Spectrom.* 252 (2006) 173–179.
- [36] B. Zhao, Z. Yang, Z. Li, M.V. Johnston, H. Wang, *Proc. Combust. Inst.* 30 (2005) 1441–1448.
- [37] S.B. Dworkin, Q. Zhang, M.J. Thomson, N.A. Slavinskaya, U. Riedel, *Combust. Flame* 158 (2011) 1682–1695.
- [38] T.S. Totton, D. Chakrabarti, A.J. Misquitta, D.J. Wales, M. Kraft, *Combust. Flame* 157 (2010) 909–914.