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Dynamic polarity of curved aromatic soot precursors

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Abstract

In this paper, we answer the question of whether polar curved aromatics are persistently polar at flame temperatures. We find, using electronic structure calculations and transition state theory, that the inversion barriers of curved aromatics (cPAH) of 0.9–1.2 nm in diameter are high and that they are not able to invert over the timescales and at the high temperatures found in sooting flames. We find a transition for smaller curved aromatics between 11–15 (≈ 0.8 nm) rings where the increasing strain introduced from the pentagonal ring increases the inversion barrier leading to rigidity. We then performed *ab initio* quantum molecular dynamics to find the molecular dipole fluctuations of a nanometre sized cPAH at 1500 K. We found the bending mode of the bowl shaped molecule gave rise to the largest fluctuations on the dipole moment by ± 0.5 –1 debye about the equilibrium value of 5.00 debye, indicating persistent polarity. We also observed binding of a chemion at 1500 K over 2 ps, suggesting the molecular dipole of cPAH will be an important consideration in soot formation mechanisms.

Keywords: soot formation, ion-induced nucleation, curved PAH inversion, buckybowl, curved PAH, polar aromatics, fullerene-like

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1. Introduction

The transformation of gas phase aromatic precursors to solid soot nanoparticles remains the most challenging aspect of soot formation [1]. The rapid second order dynamics of soot formation [2, 3] and the observation of stack mode in mass spectrometry [4, 5] suggest a physical aggregation process. The estimated size of the pericondensed aromatics in early soot nanoparticles is 0.9–1.2 nm from optical band gap measurements [6, 7, 8], Raman spectroscopy [6, 9] and laser desorption ionisation time of flight mass spectrometry [10, 11]. However, to date, rapid physical aggregation of planar polycyclic aromatic hydrocarbons (PAHs) of this size has lacked the significant interaction energies required to be stable at the flame temperatures in which soot nanoparticles form [1, 12, 13].

Aromatics that are curved due to pentagon integration have long been suggested as a precursor for soot formation [14, 15]. A small curved PAH (hereafter referred to as cPAH), corannulene (structure **1** in Figure 1), has been extracted from soot [16, 17] and the synthesis of closed cage fullerenes molecules in low pressure benzene flames have been observed [18, 19]. High resolution transmission electron micrographs have been used to suggest curvature in soot and carbon black from bent fringes [20, 21] with fringe analysis recently being used to quantify the amount (>62.5%) and degree of curvature of aromatics (1–3 pentagonal rings) in early soot particles [7, 22, 23, 24]. Curvature was suggested to be integrated through the HACA mechanism with acetylene addition to an armchair site containing a pentagonal ring [25, 26, 27, 28, 29] or oxidation of a zig zag site [30] as well as by crosslinks that rearrange into curved pericondensed structures containing internal pentagonal rings [14, 15].

At the recent 37th International Symposium on Combustion, we suggested the importance of considering the significant polarity of these cPAH species [31]. Our detailed electronic structure calculations revealed a significant electric polarisation that occurs at the strained integrated pentagons in curved PAH due to the flexoelectric effect (4–6 debye for species found in early soot) [32, 23]. Further calculations suggested that the dimerisation energy of cPAHs with 1–2 pentagons were found to be comparable to that of similar sized planar PAHs. The calculations also suggested that for a PAH to become flexoelectric more than six aromatic rings are required. Electrostatic interactions between permanent dipoles range significantly farther than dispersion interactions, suggesting an influence on the stability of early soot

38 clusters [31].

39 The interaction of cPAHs with charged species in flames is of particular
40 interest. We calculated significant binding energies between cPAH and the
41 dominant chemi-ion in sooting hydrocarbon flames, cyclopropenyl ($C_3H_3^+$)
42 (>40 kcal/mol [23]). Chemi-ions are produced in significant concentrations
43 in flames and their correlations with soot formation have long been known [33,
44 34, 35, 36], such as the impact of electric fields [37, 38, 39] and the addition
45 of alkali metal ions [40, 41, 42]. Recently, Carbone et al. [43, 5] found that
46 atmospherically sampled cations from a flat flame formed nanometre sized
47 positive clusters through physical aggregation of pericondensed aromatics,
48 while negative ions did not readily grow into nanoparticles, further indicating
49 a charge dependent growth mechanism is possible.

50 One significant issue raised at the symposium surrounding such an ionic
51 route was how persistent the polarity of curved PAH is at the temperatures
52 of sooting flames. Dynamic polarity presents two problems for interactions
53 of cPAH with each other and chemi-ions: 1) rapid inversions of cPAH would
54 likely impede their ability to form a stably bound complex, 2) fluctuations
55 of the dipole moment at flame temperatures could mean that the dipole
56 moment decreases, thereby preventing the formation of a cPAH cluster. For
57 inversion the small cPAH corannulene is well known to rapidly invert at
58 room temperature with an experimental inversion barrier of 10.2 kcal/mol
59 [44] and computed barrier of 11.5 kcal/mol [45]. This barrier is significantly
60 lower than the strain energy anticipated in corannulene 24 kcal/mol [46],
61 this lower inversion barrier was explained by the planar transition state that
62 increases π -electron delocalisation decreasing the barrier by 11 kcal/mol [47].
63 Soon after corannulene was found to invert rapidly at room temperature it
64 was also found that by addition of a single extra pentagonal ring about the
65 rim, the inversion barrier was doubled and the inversion was halted at room
66 temperature [48]. Calculations of larger cPAH have found a non-planar S-
67 shaped transition state that considerably increases the inversion barrier with
68 a one pentagon 10 ring species giving an inversion barrier of 56 kcal/mol while
69 two pentagon >14 ring species gave inversion barriers of >100 kcal/mol [49].

70 In this paper, we aim to determine the persistence of cPAHs polarity
71 at temperatures at which soot forms in a flame and study the interaction
72 of an ion with a dipolar cPAH. The rate of inversion is computed for a
73 range of cPAH revealing the size required for inhibition of inversion in flame
74 conditions. We then use *ab initio* molecular dynamics simulations to track
75 the fluctuation of the dipole moment of a cPAH and study the dynamics of

a chemi-ion interacting with the cPAH over two picoseconds.

2. Methodology

Figure 1 shows the curved PAHs chosen for this study. These include the smallest aromatic, curved by pentagon integration that we have found, corannulene **1** [31]. We then considered molecules of the size seen in early soot particles 0.9–1.2 nm; a fifteen ring structure with a single pentagonal ring and a five member bay site **2**, the same single pentagon structure with the closure of the bay site **3**, a two pentagon containing 15 ring cPAH **4** suggested from HRTEM imaging of early soot nanoparticles [23], a three pentagon containing cPAH is also provided **5**. For each of the largest cPAH we also added/removed a hydrogen to the site specified to consider the effect of a π -radical on the rate of inversion.

Figure 1: Curved PAH molecules chosen in this study with **3–5** chosen from a previous study [23].

The energies and frequencies of the minimum energy and transition state structures of the curved PAHs were computed using the hybrid density functional B3LYP/6-311+G(d,p) level of theory. This has been found to correctly describe the equilibrium geometry of curved arenes compared with crystal structures and the inversion dynamics of these systems [49]. For all geometries located by DFT, the frequencies were checked to ensure the calculation had found the appropriate minima and transition states. To obtain a more

95 accurate estimate of the energies of the minima and the transition state, sin-
 96 gle point energy calculations using the Minnesota hybrid density functional
 97 M06-2X/6-311g(d,p) were performed on the optimised geometries. This has
 98 been shown to give accurate energies for reactions involving PAHs [50]. En-
 99 ergies are reported with the zero point energy correction included.

100 The rate of inversion was calculated using canonical transition state the-
 101 ory as implemented within the THERMO package of the Multiwell software
 102 [51, 52, 53]. In this case the barriers of inversion are high and pressure depen-
 103 dence was not considered, so canonical transition state theory was considered
 104 sufficient over more sophisticated methods such as variational transition state
 105 theory and RRKM/Master Equation calculations. Due to the larger size of
 106 the 15 ring PAHs, the source code had to be modified to include more vibra-
 107 tional and rotational degrees of freedom than the default 150 implemented in
 108 Multiwell. Additionally, tunneling was not treated by the standard unsym-
 109 metrical Eckart tunneling in THERMO as the very large barriers of inversion
 110 led to some numerical difficulties with this tunneling form. Instead, tunnel-
 111 ing effects were treated by means of the Wigner correction. For the rate
 112 calculations in this work, the obtained Wigner tunneling corrections were
 113 extremely close to one, which is expected given the large reactants and high
 114 energy barriers.

115 *Ab initio* molecular dynamics (AIMD) techniques were used to study the
 116 thermal fluctuation of the cPAH. These methods have been used previously
 117 in combustion to study the dimer lifetimes of pyrene using a semi-empirical
 118 quantum theory. In Born-Oppenheimer molecular dynamics (BOMD) nuclei
 119 are approximated as classical ions with the forces on these ions computed
 120 from the electronic structure,

$$\partial E/\partial \mathbf{R} = \langle \Psi | \partial H / \partial \mathbf{R} | \Psi \rangle + \langle \partial \Psi / \partial \mathbf{R} | H | \Psi \rangle + \langle \Psi | H | \partial \Psi / \partial \mathbf{R} \rangle, \quad (1)$$

121 with the first term being the Hellmann-Feynman force and the second and
 122 third term being the "Pulay" forces [54]. BOMD performs a self-consistent
 123 field calculation to iteratively determine the electronic structure at each
 124 time step, which is prohibitively expensive. One successful approximation
 125 is ADMP that propagates the electronic structure using an extended La-
 126 grangian coupled to the nuclear positions via a fictitious mass, which signifi-
 127 cantly reduces the computational cost of such calculations. This is similar to
 128 the Car-Parrinello method, however for ADMP, the density matrix is prop-
 129 agated instead of the Kohn-Sham orbitals and atom-centred Gaussian basis

130 functions are used instead of plane wave basis functions [54]. These fea-
 131 tures of ADMP allow any hybrid density functional theory to be used to
 132 generate the density matrix and provides a better separation between the
 133 electronic and nuclear degrees of freedom. With small timesteps (<0.5 fs)
 134 it has been found to accurately follow the fully converge Born-Oppenheimer
 135 MD with vibrations and energy being independent of the fictitious mass
 136 used [54, 55, 56, 57]. Since it was implemented in Gaussian 03 it has seen
 137 applications in describing gas interactions with aromatic macrocycles [58]
 138 and recently been used to model the formation of covalent bonds between
 139 pyrene dimers [59]. A similar method using converged semi-empirical PM3
 140 simulations has also been employed in combustion research to study PAH
 141 dimerisation at flame temperatures by Schuetz and Frenklach [60], Wong
 142 et al. [61].

143 For the AIMD simulation used in this study a more economic level of the-
 144 ory, B97D/6-31G(d), was used. The hybrid density functional theory with
 145 dispersion correction B97D [62] has performed well compared with bench-
 146 mark coupled cluster calculations for cation-benzene clusters and dimers of
 147 corannulene (error <1 kcal/mol B97D/cc-pVTZ) [63, 64, 31]. For the molec-
 148 ular system **4** a dipole moment of 5.00 debye was calculated, which is slightly
 149 below ($<4\%$) the value calculated at a higher level of theory 5.32 debye [23].
 150 We calculated binding energies of 40.9 kcal/mol, which is larger than that
 151 calculated at a higher level of theory B97D/cc-pVTZ = 38.1 kcal/mol but
 152 should provide preliminary insight into the dynamics of the system [23]. In
 153 simulating the C_3H_3^+ -**4** system we found little impact of the fictitious mass
 154 on the energetics, as others have also documented [56] and therefore we made
 155 use of the default mass of 100 amu. We used a timestep of 0.1 fs to ensure
 156 energy conservation during the simulation. **A NVT ensemble was enforced**
 157 **to maintain the high temperatures found within the flame where soot forms**
 158 **(1500 K). Ergodicity was confirmed after the first ≈ 300 fs by computing the**
 159 **velocity-velocity autocorrelation function. Dynamics were only recorded af-**
 160 **ter this initial thermalisation had been performed.** No angular momentum
 161 was included in the system to provide a better understanding on the vibra-
 162 tional degrees of freedom. Gaussian 16 was used for all of the electronic
 163 structure and AIMD calculations performed in this work [65].

164 3. Results and discussion

165 3.1. Inversion of curved PAH at flame temperatures/timescales

166 To introduce the inversion process we have plotted the energies and ge-
 167 ometries of the transition state for inversion of molecules **1**, **2** and **3** (Fig-
 168 ure 2). For the smallest structure corannulene **1** the barrier was low, 11
 169 kcal/mol, due to the planar transition state as discussed earlier. Enlarging
 170 the PAH so that it was similar in size to those found in soot **2** increases the
 171 inversion barrier considerably, raising it to 59 kcal/mol. The transition state
 172 was still found to be planar for this geometry.

Figure 2: Energies and geometries of the inversion transition states.

173 Figure 3 shows the bond lengths of the equilibrium geometry and the
 174 transition state showing the considerable strain in the system. The first
 175 thing noticed was the reduction in bond lengths at the pentagonal site. For
 176 the bay site we see the considerable increase in the distance between the bay
 177 exterior carbons, 3.3 Å to 3.92 Å and a lengthening of the bonds around
 178 the baysite 1.5 Å to 1.58 Å. This flattening expands the exterior rings and
 179 compresses the interior carbon network and is consistent with strain from
 180 the σ -bonding - skeleton strain.

181 Closing the bay site of **2** to form species **3** gives rise to an almost doubling
 182 of the inversion barrier. Figure 2 shows the S-shaped transition state formed
 183 due to this bay closure. It is important to note that for the S-shaped tran-
 184 sition state the inversion still involves all core carbon atoms flipping from
 185 one side to the other. Figure 4 shows the imaginary frequency associated
 186 with the planar transition state for **2** and the S-shaped transition state for **3**.
 187 The main difference in the transition state being the warped nature of **TS3**.

Figure 3: Geometries of molecule **2** at equilibrium and at the transition state **TS2**.

188 This warping indicates the skeletal strain overcomes the π -bonding to pro-
 189 duce the S-shape. We have previously found a similar interplay of curvature
 190 vs planarity with small pentagon containing PAH [31].

Figure 4: Molecular geometries with blue arrows indicating the relative amplitude and direction of the imaginary vibrations associated with the transition states of molecules **2** and **3**.

191 Increasing the number of pentagons increases the barrier to inversion.
 192 Figure 5 shows the transition state energies and geometries for cPAH con-
 193 taining one **3**, two **4** and three **5** pentagonal rings. A modest increase is seen
 194 between one and two pentagonal rings, 114 to 138 kcal/mol, respectively. In-
 195 tegration of three pentagonal rings significantly increases the inversion barrier
 196 with molecule **5** barrier rising to 360 kcal/mol. The transition state geome-
 197 tries are heavily pyramidalised and warped with no internal carbon atoms
 198 being completely planar, thus significantly disrupting the π -bonding.

Figure 5: Inversion barriers and molecular geometries for molecules **3**, **4** and **5** as well as their π -radicals **3'**, **4'** and **5'** dashed line.

Minimal changes in the inversion barrier was seen for the π radicals compared with the closed shell structures. In the case of **TS3'** we even saw an increase in the barrier to inversion. We think this is due to the loss of hydrogen leading to an increased aromaticity and therefore stability of the transition state. This suggests that the aromaticity is more important than the π radical nature for transition states near planarity. Little change was seen for the two pentagon containing molecule's transition state **TS4/TS4'**. The most strained structure has the most significant radical effect **5** decreasing the barrier for inversion by 26 kcal/mol.

The geometries and frequencies calculated were used to compute the inversion rate for the species in Figure 1. The reciprocal of the inversion rate constant was used, $1/k = \tau$, which can be thought of as a characteristic time for inversion, as a function of the temperature. The characteristic time can be compared to the time scale of soot formation, which in a premixed flame is from micro to milliseconds [3]. Any characteristic time below a millisecond will then be important for early soot formation as above this value no inversion can occur on the time scale of soot formation. Another distinction can be made considering the temperature in the flame where soot forms which are near 1500 K [1]. Figure 6 shows that only corannulene has considerable

low temperature inversion **1**, which is a well known result experimentally verified by Scott et al. [44]. Molecule **2** is able to invert at high temperatures, however, for the other molecules and their radicals the temperature required for them to invert during soot formation timescales is too high that the molecules would breakdown before this threshold was reached.

Figure 6: Characteristic time for inversion for the species shown in Figure 1 with π -radicals shown in dashed line.

Table 1: Inversion barriers E_{inv} (kcal/mol), values from the Arrhenius fitting of the form $k = A \exp(-E_a/k_b T)$ (s^{-1} and kcal/mol), the rate of inversion at 1500 K ($cm^3 mol^{-1} s^{-1}$) and the characteristic time, $\tau = 1/k$, at 1500 K (s).

Species	E_{inv}	A	E_a	Rate at 1500 K	τ at 1500 K
1	11	3.76×10^{12}	11.2	8.62×10^{10}	11.6 ps
2	59	3.10×10^{12}	60.0	5.62×10^3	180 μs
3	114	5.64×10^{13}	116.5	5.76×10^{-4}	1737 s
3'	121	1.70×10^{13}	121.6	3.28×10^{-5}	30.5×10^3 s
4	138	1.09×10^{13}	139.6	4.74×10^{-8}	21.1×10^6 s
4'	137	1.47×10^{13}	138.7	8.65×10^{-8}	11.6×10^6 s
5	360	1.32×10^{15}	365.5	6.82×10^{-39}	0.15×10^{39} s
5'	334	8.07×10^{14}	339.3	2.69×10^{-35}	36.2×10^{33} s

In order to extend this analysis to consider the onset of rigidity in smaller

224 curved PAH we have considered the size dependency of the inversion. This
 225 was achieved by using the exponential relationship between the characteris-
 226 tic time and the barrier for inversion calculated for the species in Figure 1,
 227 to determine a barrier of 66.3 kcal/mol that would provide a characterisitic
 228 time of 1 millisecond at 1500 K. This allows us to consider the inversion
 229 barrier’s previously calculated by others at similar levels of theory [66, 67] to
 230 provide a clear picture for when inversion will be halted at flame tempera-
 231 tures/timescales of interest. Figure 7 shows the inversion barrier for different
 232 species as a function of the total number of hexagonal and pentagonal rings
 233 (from our previous study of Gaussian curvature and the integration of curva-
 234 ture [68, 31] we defined pentagons as an internal pentagon surrounded by 5
 235 hexagonal rings or an exterior pentagon that has >3 neighbouring hexagonal
 236 rings that are adjacent to each other).

Figure 7: Inversion barrier as a function of the number of rings for structures in this work and from previously studied cPAH [66, 67]. The dashed line highlights the inversion barrier 66.3 kcal/mol which provides a characteristic time of 1 ms at 1500 K from our calculations.

237 Three different size ranges were found for the inversion behaviour of peri-
 238 condensed cPAH. For $6 \leq N_{rings} < 11$ inversion occurs rapidly at flame
 239 temperature. For $11 \leq N_{rings} \leq 15$ inversion does not occur for species with
 240 ≥ 2 pentagonal rings but is possible for species containing a single pentagonal
 241 ring. For $15 < N_{rings}$ structures are stability curved during the entirety of
 242 soot formation.

243 Considering the impact of inversion on soot formation a few conclusions

can be drawn. For small curved PAH we expect that inversion is an important consideration with corannulene inverting rapidly, which will average out the flexoelectric dipolar effect. This is somewhat seen in the similar vapour pressure of perylene and corannulene [69]. Addition of rings increases the inversion barrier so that for the size of PAH seen in early soot particles the inversion is not rapid enough to be important at flame temperatures and timescales. The π -radical nature does not significantly lower the barrier for inversion indicating the skeletal strain dictates the inversion dynamics.

Further work is needed to understand the rate of inversion of cPAH inside clusters as barriers for inversion of cPAH have been found to decrease in the presence of a planar PAH [70, 71] or in different molecular environments [72]. These effects only **operate** for cPAH with planar transition states. It appears that the transition from planar to S-shaped transition states determines when the cPAH becomes rigid at flame **temperatures**. **This** can be seen in Figure 7 where the larger barriers for inversion are predominately for those species with S-shaped transition states (denoted by filled symbols).

While it seems unlikely inversion will occur for cPAH found in early soot particles the suggestion of an interaction with a chemi-ion needs to be considered to see if it can catalyse an inversion. This will be considered for molecule **4** in the presence of C_3H_3^+ . Figure 8 shows the barrier for inversion, which was lowest when going from the convex arrangement to the transition state **4+**(. The transition state energy barrier was similar, 140 kcal/mol, compared to without an ion, 138 kcal/mol, indicating the presence of the ion has a minimal effect on the inversion barrier and therefore the dynamics of the bowl.

3.2. *Fluctuations of the dipole moment*

In order to consider the fluctuations of the dipole moment of a cPAH at temperatures in the flame where soot inception occurs we have performed AIMD simulations. Due to the expense of the calculations we decided to include a chemi-ion, which allows for some insights to be gained on the impact of cPAH flexoelectric dipole at high temperatures and as the inversion dynamics are minimally impacted by the chemi-ion we can consider the cPAH fluctuations as being independent. The chemi-ion was placed on the top surface of the bowl as this is the expected binding site for an ion approaching from a large distance with the flexoelectric dipole aligning to interact with the positive charge. The simulation was run for half a picosecond in order

Figure 8: Barrier for inversion for molecule **4** in the presence of an ion.

for the thermal energy to equilibrate and stabilise after which the dynamics of molecule **4** and the chemi-ion C_3H_3^+ , $\mathbf{4}+$, were followed over 2 ps.

Figure 9 a shows the trajectory of the atomic positions over the first picosecond. Concentrating on the cPAH fluctuations we see that the carbon atoms near the middle of the aromatic plane had a reduced range of motion compared to the atoms around the rim of the cPAH. The main low frequency vibrations observed were bending mode vibrations where the edge warps. This bending modes occurred with a frequency of 250–350 fs. The local flexoelectric dipole moment changed with this vibration. Instead of calculating the dipole moment at every time step, which would have been prohibitively slow, geometries were chosen over one of these bending modes and single point energy calculations performed of the cPAH only (Figure 9b). The dipole moment at this level of theory was 5.00 D and therefore the dipole moment was found to fluctuate by ± 0.5 –1.0 debye, ± 10 –20%. This analysis showed that at temperatures in the flame where soot forms large cPAH have a persistent polarity that does not decrease substantially during thermal excitation.

The movement of the chemi-ion was then considered in the presence of the cPAH. While the ground state equilibrium geometry shows a binding site above the pyramidalised carbon atoms the chemi-ion was found to move freely across the surface from the top of the bowl to the edge of the bowl. Figure 9a shows the chemi-ion trapped at the rim of the cPAH for the first picosecond. From the electrostatics we can explain the edge binding as being

303 due to the charge concentration at the edge of the PAH from the induced
 304 dipole on the rim carbon atom caused from the C-H bond [73] and the
 305 binding to the pyramidalised atoms due to the flexoelectric dipole moment
 306 [32]. The binding of the chemi-ion does not appear to be influenced strongly
 307 by the bending mode of the cPAH as seen in Figure 9b. Figure 9c shows the
 308 movement of the chemi-ion across the top surface of the cPAH interacting
 309 with the pentagonal carbon atoms where the flexoelectric effect is greatest.

310 Further work is required on the dynamics of cPAH ion system. We only
 311 considered one cPAH chemi-ion pair, however, there are innumerable other
 312 combinations, some of which are worth considering in detail, such as the
 313 CHO+ cPAH combinations and considering smaller cPAH. We suggest that
 314 the main conclusions about dipole fluctuations we have found with molecule
 315 **4** hold for all cPAH with a large inversion barrier (>66 kcal/mol). For other
 316 ionic interactions, e.g. CHO⁺, have the potential to interact more strongly

Figure 9: Dynamics of molecule **4** and the chemi-ion. a) dynamics of the complex over the first picosecond shown with a line at each atom with the geometry at 1 ps shown with a ball and stick model. b) Fluctuation of the bowl during a low frequency bending model vibration. The dipole moment was calculated for the bowl fragment. c) dynamics of the complex over the second picosecond with the geometry shown with the ball and stick model for the final structure at 2 ps.

317 than C_3H_3^+ [13]. Additionally, as our study of chemi-ion-cPAH interactions
 318 does not capture long term dynamics for accurate statistics of the chemi-ion
 319 cPAH system we are working on developing less costly descriptions to study
 320 longer dynamics. We also did not consider the impact of rotational degrees of
 321 freedom in order for the cPAH fluctuations to be more clearly observed but
 322 this is expected to improve the binding tendencies as studies have previously
 323 found for planar PAH homodimers [60, 61]. The movement of the chemi-ion
 324 across the surface of the bowl and rim provides an opportunity for reactions
 325 with the rim carbon atoms [13]. These reactions would provide positively
 326 charged PAH, which have been observed previously using mass spectrometry
 327 [15]. The clustering behaviour of cPAH^+ with other cPAH was beyond the
 328 scope of this publication but is worth considering in future work.

329 4. Conclusions

330 To conclude, we have demonstrated that for cPAH of the size found in
 331 early soot particles (≈ 15 rings with ≈ 2 pentagonal rings) are unable to invert
 332 at flame temperatures providing persistently polar species at flame tempera-
 333 tures. The transition from being easily inverted to becoming rigid at 1500 K
 334 for cPAH was found to be between 11 and 15 rings and often corresponded
 335 to a S-shaped transition state that was not stabilised by an increased aro-
 336 maticity as with planar transition states. Π -radicals and chemi-ions were
 337 not found to influence the inversion barrier substantially with the number
 338 of pentagonal rings and total rings being of primary importance. *Ab initio*
 339 MD simulations were used to study the fluctuation of the dipole moment for
 340 molecule **4** at flame temperatures. The dipole moment was found to change
 341 on the timescale of the bending mode of the bowl, ≈ 300 fs, by ± 10 -20%.
 342 Some brief dynamics of the chemi-ion cPAH system were considered with
 343 the chemi-ion. An interaction with the pentagonal atoms with a flexoelectric
 344 effect was found as well as at the rim due to charge concentration. These
 345 results indicate that the polarity of cPAH found in early soot particles are
 346 important to consider in soot formation mechanisms.

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