The formation mechanism of polycyclic aromatic hydrocarbons (PAHs) is an increasingly important area of research due to their role in combustion, atmospheric, circumstellar, and interstellar chemistry. Incomplete combustion of fuels results in the formation of soot particles which, when released into the atmosphere, contribute to global warming and environmental damage. Inhalation and ingestion of these particles is of concern for human health due to their toxic and carcinogenic properties. PAHs are suspected to play the role of early intermediates in the soot nucleation process.

Comparably with terrestrial soot, PAHs are viewed as the initial precursors of stellar dust grains being formed in the circumstellar shells of carbon rich evolved stars. The most convincing evidence of the presence of PAHs in the interstellar medium (ISM) comes from infrared emission features termed the aromatic infrared bands (AIBs). These strong features between 3-20um are ubiquitous in the spectra of interstellar objects and are characteristic of large PAH molecules (Tielens 2013, Pech etal 2002). Modelling based on these optical observations allows the inference of chemical abundances and size distributions with an estimated 20% of the total cosmic carbon abundance locked up in PAHs of sizes 50—100 C atoms (Dwek et al 1997). PAHs are also strongly considered as carriers of the diffuse interstellar bands (DIBs) – a series of unidentified absorption features in the visible to near-infrared region – based on their stability, suspected abundance and first electronic transition (Cox 2011). Laser desorption mass spectrometry investigations of carbonaceous chondrites – Allende and Murchison – reveal a distribution of PAHs with origins pre-dating their entrance to the Earth’s atmosphere, indicating an interstellar or interplanetary origin (Plows et al 2003). Whilst no PAHs have been currently identified in the ISM, aromatic species such as benzene and benzonitrile containing a single ring, as well as the fullerenes C60, in its neutral and cationic state, and C70 have been identified in the ISM through spectroscopic techniques(Cernicharo et al 2001, McGuire et al 2018, Cami et al 2010, Campbell et al 2015). The presence of these species containing aromatic rings strongly suggests that PAHs also exist in this environment.

Due to the diversity of physical conditions within the ISM, the formation mechanism for interstellar PAHs is ambiguous. Current astrochemical models of PAH formation are predominately derived from combustion chemistry models. One popular reaction mechanism, referred to as the “bottom-up approach”, involves molecular growth processes in hot and dense circumstellar envelopes of carbon-rich asymptotic giant branch (AGB) stars (Tielens 2013). This mechanism is largely based on the hydrogen abstraction-acetylene addition (HACA) mechanism that is used to explain most PAH growth in combustion and flame experiments. The HACA mechanism was first described as an activation of a radical site by H-abstraction/addition followed by sequential addition of acetylene, finally resulting in ring closure (Frenklach et al 1984). HACA has been shown to occur experimentally for the formation of naphthalene from benzene via the phenylacetylene intermediate (Parker et al 2014, Yang et al 2016). However, there are some inherent shortcomings of this mechanism. Notably, modelling studies have reported that HACA under-predicts the concentration of PAHs in flames (Raj et al 2012). Alternate PAH formation mechanisms have been proposed in conjunction with HACA under combustion conditions to account for the deficiencies in PAH concentrations. These include the recombination of resonance stabilized radicals (RSRs) (Melius et al 1996, Miller et al 1992, Johanssen et al 2018), condensation of small PAHs(Siegmann \& Sattler 2000), phenyl addition/cyclization (PAC) (Shukla et al 2008) and methyl addition/cyclization (MAC) (Shukla et al 2010).

Interstellar shockwaves caused by supernova explosions as well as bombardment by energetic cosmic rays can cause the destruction of interstellar PAHs on a time scale of a few 10^8 yr (Micelotta et al 2010a, Micelotta et al 2010b, Micelotta et al 2011). Conversely, time scales for the injection of PAHs from stellar sources is significantly longer – 2 x 10^9 yrs. This disagreement, paired with the inadequacies of the HACA mechanism, suggests that crucial PAH growth routes are missing within the astrochemical model. The multitude of possible formation mechanisms may involve combustion-like conditions within circumstellar envelopes or even low temperature, low density interstellar environments such as cold molecular clouds.

Acenaphthylene (C12H8) is a molecule of relevance within combustion models as it is considered the first significant island of stability “pulling” the HACA sequence forward (Frenklach \& Mebel 2020). Theoretical investigations of the reaction between 1-naphthyl radical (C10H7dot) and acetylene at elevated temperatures above 1000 K show predominant formation of acenaphthylene (C12H8) over phenanthrene and anthracene (C14H10). Rapid cyclization after the addition of a single acetylene molecule adjacent to the bay region of a PAH to form a five-membered ring occurs much faster than the addition of a second acetylene, followed by cyclization to form a third aromatic ring (Kislov et al 2013). It was shown that PAHs with exclusively six-membered rings only accounted for up to 6/% of the total yield from the reaction of naphthalene and acetylene, with most products containing a five-membered ring (~75%). Hence, a mechanism converting a five-member ring on the edge of a PAH molecule to a six-member ring is necessary to explain reaction pathways to tricyclic and larger PAHs.

Ring expansion has been thoroughly investigated for an isolated five-member ring, the cyclopentadienyl radical (C5H5dot) (Melius et al 1996, Moskaleva et al 1996, Sharma et al 2009), and a five-member ring attached to benzene, the 1-indenyl radical (Mebel et al 2016, Jasper and Hansen 2013, Zhao et al 2019). This reaction can readily occur by methylation (addition of a CH3 radical) to form benzene and naphthalene, respectively. Recently, ab initio calculations in combination with RRKM-ME calculations for the reaction of 1-acenaphthyl (C12H7dot) and methyl (CH3dot) radicals show ring expansion of the five-member ring by formal insertion of a CH2 group into a C—C bond and subsequent isomerization to produce the phenalenyl radical (C13H9dot) (Porfiriev et al. 2020). The phenalenyl radical is an open-shell, neutral, RSR consisting of three benzene rings fused together by a central carbon atom. It is considered a prototypical open-shell graphene fragment (Morita et al 2011) and is posited to have a role in soot inception and growth based on vacuum ultraviolet aerosol mass spectrometry studies (Johanssen et al 2018). The gas phase, resonance enhanced multi-photon ionisation (REMPI) spectrum for the D0 🡨 D1 state of the phenalenyl radical has been previously recorded with an origin at 18800 cm-1 (O’Connor et al 2011). The methylation mechanism proposed by Mebel and co-workers has not been experimentally proven to occur for PAHs containing a five-membered ring on a zigzag edge as is the case for acenaphthylene.

Ring expansion of a five-member ring to a six-member ring has also been demonstrated through the reaction of pyrrole (C2H5N) with methylidyne radical (CH) to form pyridine (Soorkia et al 2010). The CH radical in its X2pi ground state has been detected in combustion environments (Love et al 2011, Tinaut et al 2011, Zhang et al 2012), the interstellar medium (Gerin et al 2010) and under plasma conditions (Zhou \& Fisher 2006). It also plays an important role in the photochemistry of the atmosphere of Titan, the Saturnian moon (Krasnopolsky 2009). The CH radical is one of the most reactive hydrocarbon radical species due to the presence of one singly occupied and one vacant non-bonding molecular orbital localized on the carbon atom (Goulay et al 2009). Reactions between the CH radical and small unsaturated hydrocarbons and carbonyls has been shown to result in CH insertion to the C—C pi-bond (Goulay et al 2009, Trevitt et al 2013, Goulay et al 2012). In general, the CH radical adds to a C—C double bond to form a cyclic intermediate (cycloaddition) that immediately isomerizes through ring opening (Trevitt \& Goulay 2016). Isotopomer distribution experiments provided additional evidence for this cycloaddition mechanism through the reactions of deuterated methylidyne radical (CD) with ethylene and pyrrole (Goulay et al 2009, Soorkia et al 2010).

In this work, we experimentally investigate the ring-expansion PAH growth mechanism from acenapthylene to the phenalenyl radical. Acenapthylene and methane (CH4) molecules interact, and subsequent radical gas-phase reactions are induced by means of an electrical discharge. This allows for the simultaneous examination of the methylation mechanism, championed by Mebel and co-workers, as well as the cycloaddition mechanism suggested by Trevitt \& Goulay. Reaction products and intermediates are identified using the mass selective REMPI technique in conjunction with isotope labelling experiments. Although conditions are not completely analogous with combustion conditions, nor interstellar environments, reaction routes occurring in the discharge are of interest for both combustion and astrochemistry as possible growth pathways for PAHs.