

Photofragmentation of coronene cations

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Abstract. Recent laboratory studies have shown that PAH cations dehydrogenate to give charged molecules consisting of only carbon atoms. Our experiments using ion-trap time-of-flight mass spectrometry show that a key group of photodissociation fragments from the coronene cation ($C_{24}H_{12}^+$) are carbon clusters of C_n^+ composition. Density functional theory calculations shed light onto potential dissociation pathways leading up to the main C_{11}^+ and C_{12}^+ clusters, and highlight the importance of pentagon formations in the carbon backbone of the precursor molecule in generating certain fragments.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) lock up 15% of all interstellar elemental carbon and are known to influence the local physical and chemical conditions of the interstellar medium (ISM) (Tielens (2008)). Interaction with UV photons in interstellar radiation fields can lead to modifications in the chemical composition and structure of a PAH, as well as fragmentation. Recent experiments using time-of-flight photo-ionisation mass spectrometry have revealed that extensive photo-processing of PAH cations causes them to dehydrogenate and ultimately form charged species that are comprised of only carbon atoms likely organised in a ring or cage structure (West *et al.* (2014); Zhen *et al.* (2014a,b)). The complete dehydrogenation of PAHs, triggered by UV photolysis, has been shown to initiate pentagon formation in the molecule, leading to structural irregularities and curling of the carbon skeleton (de Haas *et al.* (2017)). Here, we use time-of-flight mass spectrometry alongside density functional theory to study the photo-stability of the coronene cation ($C_{24}H_{12}^+$) and investigate the importance of dehydrogenation and pentagon incorporation in the pathways to form smaller carbonaceous species.

2. Methods

Experiments were performed on our custom-made mobile Instrument for the Photodynamics of PAHs (i-PoP), consisting of a quadrupole ion-trap (QIT) and a reflectron time-of-flight (reTOF) mass spectrometer (Zhen *et al.* (2014a)). Coronene ions are generated by electron ionisation and transported into the QIT *via* electrostatic lenses, where they are trapped in a radiofrequency field. Helium is admitted to the ion trap to thermalise the ion cloud. Mass-selected ions are irradiated by multiple (up to 35) pulses from a Nd:YAG pumped dye laser, resulting in fragmentation of the coronene cations. The fragments are led into a reTOF mass spectrometer and analysed. Ancillary density functional theory calculations were performed using the supercomputer LISA at SURFsara to guide our interpretation of the experimental spectra.

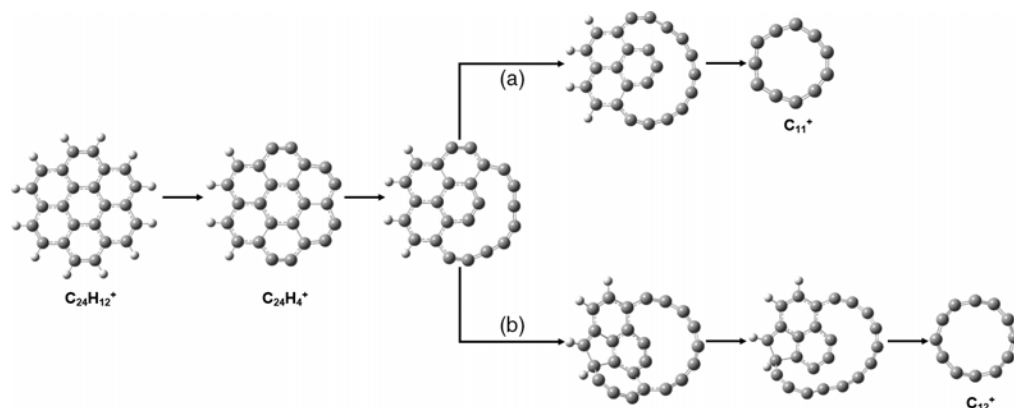


Figure 1. Molecular dissociation pathways to (a) C_{11}^+ and (b) C_{12}^+ .

3. Results and Conclusions

The mass spectrum resulting from the laser-induced dissociation of coronene cations shows a distribution of peaks corresponding to the loss of hydrogen atoms. Furthermore, mass peaks relating to dissociation products in which the carbon backbone consists of 11 up to 15 C atoms are observed at $m/z = 132, 144, 156, 168$ and 180 . The most intense peak at $m/z = 132$ is attributed to the carbon cluster of C_{11}^+ composition, observed only after the loss of 8 hydrogen atoms from $C_{24}H_{12}^+$. After increased laser exposure, the peaks corresponding to larger carbon clusters, *i.e.* C_{12}^+ to C_{15}^+ , also arise.

Possible dissociation pathways of the first two clusters, C_{11}^+ and C_{12}^+ , were obtained using DFT calculations (Fig. 1). C_{11}^+ can form through the straightforward breaking of three internal carbon-carbon bonds from the partially dehydrogenated $C_{24}H_4^+$ intermediate. The formation of C_{12}^+ relies on the incorporation of pentagons *via* a 6-6 \rightarrow 5-7 ring isomerisation to include an additional carbon atom in the resulting "exploded" chain. These mechanisms are thought to extend to the larger carbon clusters observed, with C_{11}^+ serving as an analogue for clusters with an odd number of carbon atoms, and C_{12}^+ for those with an even number. Both fragments energetically favour adopting a ring over a linear chain conformation.

We highlight here the necessity to consider the inclusion of pentagons in the formation of key fragments from the photodissociation of PAHs. We hypothesise that these pentagons may also be crucial in determining the structures of the low-mass hydrocarbon fragments (<120 amu), and hold the key to further our understanding of the dissociation characteristics of interstellar PAHs at a molecular level.

References

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