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Interactions of energetic ions with fullerenes, PAHs, and their weakly bound clusters

Henning Zettergren

Department of Physics, Stockholm University, Albanova University Center, SE-10691 Stockholm, Sweden

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ABSTRACT

This brief review highlights recent advances in our understanding on how fullerenes, Polycyclic Aromatic Hydrocarbons (PAHs), and their clusters respond to singly and multiply charged keV-ion impact. These studies reveal how the projectile charge, mass, and velocity may be tuned to investigate, e.g., the stabilities of multiply charged monomers and clusters, different monomer and cluster cooling processes, molecular heating by Coulomb explosions of highly charged clusters, and impulse driven molecular growth processes.

1. Introduction

In 1985, Kroto et al. [1] discovered a new form of carbon in an experiment where graphite was vaporised by laser irradiation. These so-called fullerenes contain an even number of carbon atoms bound in the form of closed, three-dimensional cages. Due to their exceptional stabilities, Kroto et al. [1,2] suggested that they should be omnipresent in the Universe. Indeed, fullerenes have been shown to be efficiently produced from carbon-rich vapours in a large variety of ways in the laboratory as well as in nature (e.g. in sooting flames). However, it took twenty-five years before they were identified in space. In 2010 Cami et al. [3] reported observations of the characteristic IR-emission features from C_{60} and C_{70} from a young planetary nebula. Recently, Maier and coworkers [4,5] identified C_{60}^{+} as a carrier of four of the more than four hundred so called diffuse interstellar bands [6], thus confirming the initial suggestion by Kroto et al. [1,2,7].

Despite strong research efforts, it is still an open question how fullerenes are formed in man-made and naturally occurring situations. However, it is likely to be dependent on the actual conditions in the environment where they are born. In the interstellar medium, it has been suggested that they may be formed from UV-pumped large Polycyclic Aromatic Hydrocarbons (PAHs) [8,9]. This class of molecules typically contain planar hexagonal carbon structures, which are fused like small pieces of graphene and decorated by hydrogen atoms around their exterior perimeters. PAHs are believed to be omnipresent in space as their IR-emission features match those from many astronomical objects [10–14]. No single PAH structure has yet been identified as they all display similar IR-signatures, but PAHs in space are generally believed to contain more than fifty carbon atoms to survive in such harsh environments [13]. These examples highlight the importance of understanding how energetic processing affects the formation, survival, and destruction of fullerenes and PAHs. Another key question concerns the role of a surrounding environment (e.g. small clusters or dust grains) in these processes.

Fullerenes and PAHs form weakly bound clusters (see Fig. 1) where the binding energies are significantly smaller (less than 1 eV) than those within the individual building blocks ($\gtrsim$ 4 eV for PAHs [15,16] and $\gtrsim$ 10 eV for fullerenes [17,18]). As a consequence, clusters predominantly emit neutral intact molecules when internally heated rather than molecular fragments [19]. In the latter case, the lowest dissociation energy pathways are H-loss, H_2-loss, and C_2H_2-loss for PAHs [13] and C_2-loss for fullerenes [20,21], which are typically observed when *isolated* molecules are internally heated by ions, atoms, electrons, or photons. Such fragmentation processes are statistical in the sense that the energy is redistributed across all degrees of freedom before the decay. However, this is not always the case for ion-impact where localized interactions may favour unexpected fragmentation pathways with significantly higher activation energies ($\gtrsim$ 25 eV) than those with the lowest dissociation energies [22].

E-mail address: henning@fysik.su.se

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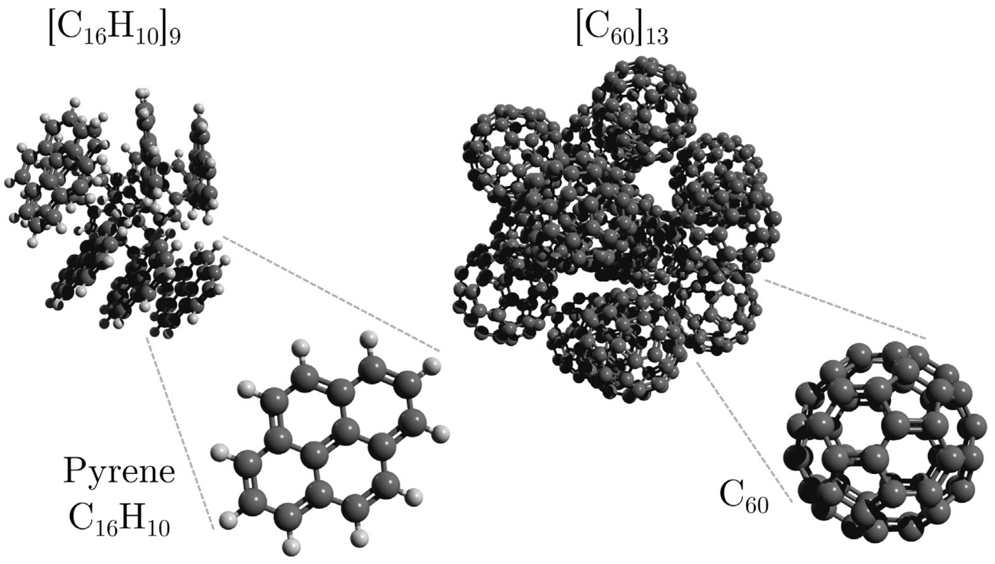

Fig. 1. Examples of weakly bound clusters of Polycyclic Aromatic Hydrocarbons (here $C_{16}H_{10}$) and fullerenes (C_{60}).

In this review, we highlight results from keV-ion impact on fullerenes, PAHs, and their clusters. We aim to give the reader an overall picture of such interactions with focus on highly charged projectiles. In Section 2, we present results from studies of charge and energy flow processes in collisions with monomer targets. The effects of a surrounding (cluster) environment is discussed in Section 3.

2. Collisions with monomer targets

2.1. Charge transfer in distant collisions

In 1994, Walch et al. [23] demonstrated that multiply charged fullerenes, C_{60}^{q+} ($q \leqslant 6$) were efficiently produced in 80 keV $Ar^{8+} + C_{60}$ collisions. These were attributed to distant electron transfer collisions where little energy is deposited due to direct interactions with the molecular electron cloud (electronic stopping) and nuclei (nuclear stopping). Such collisions have been successfully described with the aid of a quasimolecular approach [24,25] and models based on the classical over-the-barrier concept [26–29]. In the latter models, an electron is classically allowed to transfer to the projectile when the maximum of the potential energy barrier for the active electron becomes lower than its Stark-shifted binding energy to the fullerene target. At such charge transfer distances, C_{60} may be accurately treated as a metal sphere [29] according to Density Functional Theory (DFT) calculations [30].

The pioneering work by Walch et al. [23] was followed by a vast number of studies investigating multiply charged fullerenes (see e.g. [29,31–48,25]). These showed for instance that emission of neutral fragments are the dominant fragmentation pathways for fullerenes in low charge states, while multiply charged species predominantly decay by emission of charged fragments. The latter determines the ultimate Coulomb stability limit, which according to DFT calculations is $q = 14$ for C_{60} [49]. These calculations further showed that multiply charged fullerenes are metastable for $q \geqslant 6$, and that there is a so called fission barrier (transition state) which determines their lifetimes. The highest observed charge state is $q = 10$ for ion impact [44], i.e. somewhat lower than predicted by the DFT calculations [49]. One possible reason for this difference is that the multiply charged fullerenes are born in their neutral geometry (vertical ionization) and that the relaxation energy is sufficient to overcome the fission barrier in such cases. Interestingly, C_{60}^{12+} has been observed by intense (10^{15} W cm^{-2}), short (70 fs) infrared (1800 nm) laser pulses [50], suggesting that they may be produced with lower internal energies with photons than in collisions with ions.

In 2011, Ławicki et al. [51] reported the first study on collisions between highly charged keV-ions and PAH monomers (pyrene and coronene). In Fig. 2 we show the mass spectrum they recorded for 300 keV $Xe^{20+} + C_{24}H_{12}$ collisions [51]. The most prominent peaks are due to formation of intact charged molecules produced in distant electron transfer collisions, while the distribution of small fragment ions stem from smaller impact parameters in which the molecules become highly charged and Coulomb explode and/or are strongly heated in electronic and nuclear stopping processes. A zoom-in of the mass spectrum reveals the formation of $C_{24}H_{12}^{5+}$ (see Ref. [51]), the highest charge state ever observed for a PAH molecule. For the smaller PAHs anthracene ($C_{14}H_{10}$) and pyrene ($C_{16}H_{10}$), the highest observed charge state is $q = 4$ for collisions with highly charged ions [51,52].

In Fig. 3 we show dissociation energies from DFT calculations for emission of H, C_2H_2, H^+, and $C_2H_2^+$, as functions of the PAH

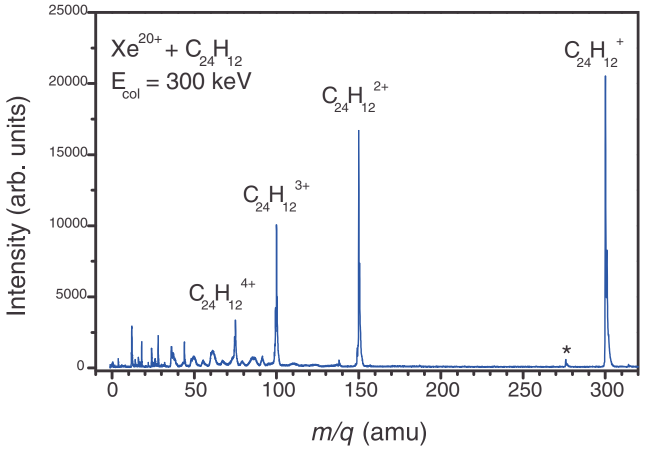

Fig. 2. Mass spectrum due to 300 keV $Xe^{20+} + C_{24}H_{12}$ collisions showing that multiply charged PAHs may be efficiently formed. Reprinted figure with permission from Ref. [51]. Copyright 2011 by the American Physical Society.

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