Ions colliding with molecules and molecular clusters: fragmentation and growth processes

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Abstract

In this work we will discuss fragmentation and molecular growth processes in collisions of Polycyclic Aromatic Hydrocarbon (PAH) molecules, fullerenes, or their clusters with atoms or atomic ions. Simple collision models as well as molecular structure calculations are used to aid the interpretations of the present and other experimental results. Fragmentation features at center-of-mass collision energies around 10 keV are dominated by interactions between the fast ion/atom and the electron cloud in the molecules/clusters (electronic stopping processes). This electronic excitation energy is rapidly distributed on the vibrational degrees of freedom of the molecule or of the molecules in a cluster and may result in fragmentation. Here, the fragmentation is statistical and favors the lowest-energy dissociation channels which are losses of intact molecules from clusters, H- and C2H2-losses from isolated PAHs, and C2-loss from fullerene monomers. We will also discuss the possibility of formation of molecular H2 direct from native PAHs which reach high enough energies when interacting with ions, electrons, or photons.

For the experiments at lower center of mass collision energies (∼ 100 eV) a single atom may be knocked out in close atom-atom interaction. Such non-statistical fragmentation are due to nuclear stopping processes and gives highly reactive fragments which may form covalent bonds with other molecules in a cluster on very short time scales (picoseconds). This process may be important when considering the formation of new species. For collision between 12 keV Ar2+ and clusters of pyrene (C16H10) molecules, new molecules, e.g. C17H10+, C30H18, C31H19, etc are detected. We also observe molecular fusion processes for He and Ar ions colliding with clusters of C60 molecules. These and related molecular fusion processes may play a key role for understanding molecular growth processes under certain astrophysical conditions.
to Xiaoyu
List of Papers

The following papers, referred to in the text by their Roman numerals, are included in this thesis.

PAPER I: **Formations of Dumbbell** $\text{C}_{118}$ **and** $\text{C}_{119}$ **inside Clusters of** $\text{C}_{60}$ **Molecules by Collision with alpha Particles**


DOI: [10.1103/PhysRevLett.110.185501](https://doi.org/10.1103/PhysRevLett.110.185501)

PAPER II: **Ions colliding with clusters of fullerenes-Decay pathways and covalent bond formations**


DOI: [10.1063/1.4812790](https://doi.org/10.1063/1.4812790)

PAPER III: **Non-statistical fragmentation of PAHs and fullerenes in collisions with atoms**


PAPER IV: **Non-statistical fragmentation of large molecules**

M. H. Stockett, H. Zettergren, L. Adoui, J. D. Alexander, U.
PAPER V: Absolute fragmentation cross sections in atom-molecule collisions: Scaling law for non-statistical fragmentation of polycyclic aromatic hydrocarbon molecules


DOI: 10.1063/1.4881603

PAPER VI: Formation of H₂ from internally heated Polycyclic Aromatic Hydrocarbons: Excitation energy dependence


DOI: 10.1063/1.4917021

PAPER VII: Molecular growth inside polycyclic aromatic hydrocarbon clusters induced by ion collisions


DOI: 10.1021/acs.jpclett.5b00405

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Articles not included in this thesis are listed in Appendix.
Author’s contribution

For Paper I-IV, I have modeled the electronic and nuclear stopping processes following collisions between atoms/ions and PAH/fullerene molecules/clusters. I have also calculated the molecular structures and electron density distributions by using quantum chemical methods.

For Paper V, I have calculated the electronic and nuclear stopping energies for various collision systems. I have derived a simple scaling law for estimating non-statistical fragmentation cross sections. I have also analyzed the experimental data and produced the model data. I drafted the publication and made all figures.

For Paper VI, I have calculated the dissociation energies for single H-emission, sequential H-emissions (H+H) and H\textsubscript{2}-emission from several PAHs, and transition barriers for H\textsubscript{2}-emission from PAHs. I drafted the publication and made all the figures.

For Paper VII, I have participated in the experimental study of the molecular growth process and contributed with calculations of energy transfers through electronic stopping processes. I have participated in discussions of the results and their interpretations.

This thesis is partly based on my licentiate thesis "Statistical and Non-statistical fragmentation of large molecules in collisions with atoms".
Sammanfattning

I denna avhandling presenteras resultat rörande sönderfall- och tillväxtprocesser efter kollisioner mellan fulleren-molekyler, PAH-molekyler (polycycliska aromatiska kolväten) eller kluster av dessa, och atomer eller atomära joner. Två olika experimentella uppställningar har använts, en för höga collisionsenergier (> 10 keV i masscentrumsystemet) och en för låga collisionsenergier (< 1 keV i masscentrumsystemet). De experimentella resultaten diskuteras och tolkas med hjälp av en kollisionsmodell, molekylära struktureräkningar och molekyldynamik-simueringar.


Icke-statistiska sönderfallsprocesser är processer i vilka enskilda kolatomer slås ut från PAH-molekyler eller fullenerer i Rutherford-liknande spridningsprocesser. Vi har observerat icke-statistiskt sönderfall i experiment där vi kolliderat PAH-/fulleren-molekyler med atomer vid låga (< 1 keV) collisionsenergier. Vi har utvecklat enkla samband för att beräkna absoluta tvärsnitt för icke-statistiskt sönderfall av molekyler.

I kollisioner mellan keV-joner och molekylära kluster spelar de snabba icke-statistiska sönderfallsprocesserna en nyckelroll i bildandet av nya molekyler. De fragment som skapas genom icke-statistiskt sönderfall är oftast mer reak-
tiva än de som bildas i statiska sönderfallsprocesser. Detta leder till att de reaktiva fragment som skapas i kollisionerna kan bilda nya kovalenta bindningar med andra molekyler i klustren. Vi har utfört experiment där vi kolliderat olika atomära joner med kluster av C\textsubscript{60} eller pyren (C\textsubscript{16}H\textsubscript{10}). I fallet med fulleren-kluster såg vi att den hantelformede C\textsubscript{119}-molekylen bildades. Med PAH-kluster skapades en rad nya molekyler med formen C\textsubscript{16+m}H\textsubscript{x}, där m = 1-21.
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References
1. Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) contain only carbon and hydrogen atoms (C\textsubscript{m}H\textsubscript{n}). They typically have three or more fused benzene-like rings. An example of a PAH molecule, pyrene is shown in Figure 1.1a. Pyrene (C\textsubscript{16}H\textsubscript{10}) has a planar structure with four benzene-like rings fused together. PAHs are ubiquitous and abundant on Earth and in Space. On Earth, it has been commonly found in combustion products of organic materials [59]. In space, many observations suggest that PAHs are present in meteorites [44], in comets [38], and in the interstellar medium (ISM) as the carriers of the strong infrared emission features from galactic and extragalactic objects [6, 65, 68, 69]. Another related class of molecules are the fullerenes, which contain only carbon atoms, and have hollow spherical structures. An example of a fullerene with 60 carbon atoms (C\textsubscript{60}) is shown in Figure 1.1b. This molecule has been unambiguously identified in space [10, 62, 79]. A recent study suggests that fullerenes could be formed from PAHs in space by multistep dehydrogenation and fragmentation processes [5].

Figure 1.1: Internally heated molecules (a. pyrene, b. C\textsubscript{60}) may cool by emitting photons, electrons, and/or molecules or atoms.

When internally heated, PAHs predominantly fragment by emitting H-atoms or C\textsubscript{2}H\textsubscript{2}-molecules which correspond to the lowest-energy dissociation channels. It is much more difficult to remove a single C-atom which is re-
flected in the fact that the corresponding dissociation energy is much higher than for H- or C2H2-loss. Similarly, the fullerenes have C2-loss as their lowest dissociation channel while the removal of a single C-atom is much more energetically unfavourable. The fullerenes have been extensively investigated both experimentally and theoretically - see for examples [13, 31, 35, 72, 78]. Larsen et al performed a pioneering experiment on the fragmentation of C60 anions in 50 keV collisions with rare gas targets. There, they observed two different types of fragmentation processes: weak direct "knock-out" processes of single C-atoms and strong delayed (statistical) fragmentation process, which are dominated by C2 emission [35]. However, it is in general hard to distinguish the knock-out and statistical fragmentation processes for large and complex molecules. Due to the three-dimensional hollow sphere structure, the signature of a direct knock-out process namely the loss of a single C atom is often disguised by secondary (statistical) fragmentation process and also by additional knock-out processes. The latter are more likely for three than for two-dimensional molecular structures. Attention has therefore be given to PAH molecules, which have planar, simple and regular structures. A vast number of studies [15, 27, 29, 36, 47, 53, 58] have been performed on excitation of PAHs by absorption of photons [24, 40], by interaction with energetic electrons [25], or atoms [9]. In a pioneering work, Postma et al studied the fragmentation of the PAH molecule anthracene (C14H10) in collisions with protons and helium ions at keV energies. They introduced a method to calculate the molecular excitation due to electronic stopping, in which the electron densities are obtained by means of Density Functional Theory (DFT). In both their experiments and their model simulations it was found that the fragmentation increased with increasing projectile velocity [53]. Reitsma et al studied the fragmentation of anthracene due to double ionization by 5 keV protons and found clear experimental evidence for dominance of C3H2+ over C2H2+ in this particular case [58]. However, Johansson et al found that C2H2-loss was the lowest energy dissociation channel for singly charged anthracene molecules [29]. Mishra et al were interested in the electron emission and electron transfer processes in proton-naphthalene collisions at velocities between 1.41 and 2.68 au. They found that electron capture cross sections decrease rapidly over the corresponding energy range [47].

The study of PAHs and fullerenes is also a hot topic in astronomy. Recent investigations suggest that molecular hydrogen (H2) could be formed from PAHs, in which the PAHs in some potential schemes may act as catalytic centers [2, 8, 12, 26, 45, 52, 64]. Figure 1.2 shows three possible routes leading to molecular hydrogen formation from a coronene molecule. In the first case (Fig. 1.2a), a coronene molecule captures a hydrogen atom to form an aliphatic carbon. This step is exothermic and the barrier for emitting a H2...
Figure 1.2: Three possible routes for the formation of H₂-molecules from PAH molecules. The examples shown are for coronene C_{24}H_{12}. In processes a, and b, the coronene molecule acts as a catalytic center absorbing one or two hydrogen atoms, respectively. In c, the H₂ molecule is formed directly from pristine coronene molecules (see the text for more details).
molecule from the aliphatic carbon is very low [34, 57]. In the second case (Fig 1.2b.), the coronene with an aliphatic carbon can lead to the formation of H$_2$ without adding a second H-atom. This however, requires that a substantial amount of energy is transferred to the system as the corresponding activation barrier is high. There is another possible route, in which the H$_2$ molecule could be formed directly from a fully aromatic PAH as shown in Fig 1.2c. It has been shown experimentally [74], that the last route is an inefficient process for singly charged PAHs with low internal energy (i.e. close to the dissociation threshold). In this work, we focus on the latter route and calculate dissociation and transition state energies for H- and H$_2$-emission from the naphthalene (C$_{10}$H$_8$), and the PAHs anthracene (C$_{14}$H$_{10}$), pyrene (C$_{16}$H$_{10}$) and coronene (C$_{24}$H$_{12}$). This work demonstrate that H- and H$_2$-formation from PAHs are two competing process. For high energy collisions (center of mass energy higher than 10 keV), the internal PAH temperatures typically exceed 2200 K and H$_2$ molecules may then be efficiently formed (see Paper VII for details).

We have also studied reaction within clusters of molecules. In all cases these molecules are weakly (< 1 eV) bound to each other through weak (e.g. van der Waals) forces. Two examples of clusters - pyrene and fullerene clusters are shown in Figure 1.3. PAH and fullerene clusters have been suggested to be omnipresent in nature [5, 7, 14, 18, 56, 68]. Many experiments and theoretical works have dealt with clusters of PAHs and fullerenes [28, 30, 72, 78]. Holm et al reported the first experimental study of keV ions interacting with clusters of PAH molecules. They found that anthracene clusters easily fragment in the collisions just like many other weakly bound clusters [28]. Johansson et al then investigated the ionization and fragmentation of anthracene and coronene clusters with similar experimental techniques as Holm et al. They found that singly charged and internally rather cold monomers are dominant products when PAH clusters fragment due to collisions with keV ions [30]. In this work, we present experimental evidence for the formation of so called dumbbell fullerene systems (see Paper I), and molecular growth of PAHs inside clusters (see Paper VII), which are ignited by non-statistical knockout processes. The cluster environment is essential here as it helps to cool the fragments such that they have time to react with neighbouring molecules in the cluster before they fragment further.

This work focuses on fragmentation processes of PAHs or fullerenes following collision with energetic ions or atoms. In general there are two different fragmentation processes (see Paper IV for details): statistical fragmentation refer to processes in which there is time for a given excitation energy to be distributed over all the internal degrees of freedom in the molecule before fragmentation. Such processes favour the lowest-energy dissociation channels. The emissions of C$_2$ molecules from fullerenes [35] are typical examples
Figure 1.3: Cluster of pyrene (a) and fullerene (b). The pyrene cluster contains four pyrene molecule, and the fullerene cluster includes five $C_{60}$ molecules. The structures were optimized using the semi-empirical PM6 method as implemented in Gaussian09 \[23\].

of statistical fragmentation processes. Examples of non-statistical fragmentation processes are processes in which atoms are knocked-out directly from the molecule in head-on collision between atomic ions or atoms and individual atoms in the molecules. Such knockout processes are fast (femtosecond timescales) and there is no time for the excitation energy to redistribute itself over all the degrees of freedom of the molecule before the initial fragmentation step. Micelotta et al simulated the interaction between interstellar PAHs and plasma shock waves from supernova explosions and concluded that non-statistical fragmentation is an important destruction mechanism: interstellar PAHs (number of carbon atom $N_C = 50$) do not survive in shocks with velocities greater than 100 km s$^{-1}$ and larger PAHs ($N_C = 200$) are destroyed for shocks with velocities $\geq 125$ km s$^{-1}$ \[46\]. Similar fragmentation processes have been unambiguously observed in experiments at center of mass energies from about 100 eV and up to about 1 keV for interaction between PAHs or fullerenes and atoms, in which single atoms are lost from the molecules. This leads to the formation of highly reactive fragments.

Statistical and non-statistical fragmentation processes often compete. After knockout, the molecule may still have high enough internal energy to decay further in secondary statistical fragmentation steps. In general, the balance between processes in which energy is transferred to the electronic degrees of freedom (electronic stopping processes) and processes in which energy is transferred directly to the vibrational modes (nuclear stopping processes) affects the balance between statistical and non-statistical fragmentation processes. Figure 1.4 shows the ratio between electronic and nuclear stopping as a function
of projectile energy for helium atoms colliding with anthracenes in solid phase \[80\]. One can see from Figure 1.4 that nuclear stopping is more important for ion energies lower than \(\sim 2\) keV, while the electronic stopping becomes more important at higher energies (> 2 keV). In order to study both fragmentation processes the present work covers the energy range from roughly 100 eV to 100 keV (gray area in Fig 1.4).

![Figure 1.4: The nuclear and electronic stopping energies as functions of projectile ion energy in the case of helium atoms colliding with anthracene in the solid phase \[80\]. The gray area indicates the energy range of main interest for the present work.](image)

The remainder of this thesis is organized as follows: In Chaper 2 the experimental technique is described for studies of PAH or fullerene monomer cations and different noble gases at center of mass energies from about 100 eV to 1 keV. In the same chapter we describe the experimental technique used for collision experiments with atomic projectiles with kinetic energies in the range above 10 keV and neutral PAH or fullerene monomers or their clusters. The theoretical calculations and the Monte Carlo simulations of electronic and nuclear stopping processes are discussed in Chapter 3. The results on \(\text{H}_2\) formation, the simple scaling law for non-statistical fragmentation and molecular growth processes are discussed in Chapter 4. Finally, concluding remarks and an outlook are given in Chapter 5.
2. Experimental techniques

This section describes two complementary experimental setups for studies of fragmentation and molecular growth processes in collisions between ion/atoms and molecules or molecular clusters. The setup at Stockholm University is utilized for low energy (< 1 keV) Collision Induced Dissociation (CID) experiments of molecular ions, where nuclear stopping is the dominant energy transfer process in the collisions (see Figure 1.4). The setup in Caen, France, is utilized for higher energy (> 10 keV) collisions. There, electronic stopping is more important than nuclear stopping (see Figure 1.4).

2.1 Collision induced dissociation experiments with PAH and fullerene cations

The experimental setup at Stockholm University is a part of the DESIREE facility \[61\ 67\] and is designed for low energy collisions between molecular ions/anions and neutral gases (atoms and molecules) and for studies of interactions with laser photons. A schematic of the experimental setup is shown in Figure 2.1. The molecules under study are dissolved in a solution and brought into gas phase by means of electrospray ionization \[19\ 76\]. In this technique, the needle of a syringe carrying the solution is kept at a high voltage (2-3 keV) to create a strong electric field between the needle and a capillary serving as a counter electrode. The syringe plunger is then pushed at a controllable rate such that charged droplets are ejected from the top of the needle \[50\]. The temperature of the capillary may be adjusted for evaporation of unwanted solvent molecules \[77\].

The so formed isolated molecules leave the capillary and enter a radio-frequency ion funnel \[32\ 33\ 63\]. The ion funnel focuses the ions into two sets of octopoles \[66\] used to accumulate the ions in bunches (not used in the present work), and to guide the ions to a quadrupole mass filter \[51\].

The quadrupole mass filter is used to mass-to-charge select ions for the primary projectile beams for the experiments. The mass-selected PAH cations enter a quadrupole deflector before they leave the high-voltage platform, are accelerated and enter the experimental beam line which is at ground potential. The accelerated ions are guided to the collision chamber by means of
**Figure 2.1:** Schematic of the experimental setup used for collision induced dissociation (CID) type experiments at Stockholm University. The molecular ions are produced by means of electrospray ionization, collected by an ion funnel, guided by two octopoles, mass-selected by a quadrupole mass filter, and accelerated before entering the collision cell. There they collide with a target gas and the so formed fragments are analyzed by means of electrostatic deflectors and a micro-channel plate detector with a resistive anode (see text).

**Figure 2.2:** Normalized count rates of the primary PAH$^+$-beams as functions of gas cell pressure for different PAHs colliding with He at 110 eV center-of-mass energy. The slope of the fitted lines yield the total fragmentation cross sections. The pressure is measured by means of a capacitance manometer. Statistical errors are smaller than the data points.
an einzel lens and deflector elements to enter a 4 cm long collision cell. The absolute pressure of the target gas in the collision cell is measured with a capacitance manometer and the pressure may be adjusted in a controlled manner by a needle valve. The beam intensity for keV-ions entering the collision cell is typically a few thousands of ions per second. The intact PAH cations and fragment ions leaving the collision cell are mass-to-charge analyzed by means of two sets of electrostatic deflectors and focused by means of an einzel lens. The ions are then detected by a micro-channel plate (MCP) equipped with a resistive anode for position information. The position information is stored for each collision event together with the corresponding deflector and lens settings. This may be used to achieve the necessary resolution in the mass spectrum without using slits in front of the detector.

The beam attenuation method [71] was used to determine absolute fragmentation cross sections. The ion beam count rate is then measured as a function of the gas pressure in the cell. Figure 2.2 shows such trends for different PAH cations colliding with He at 110 eV center of mass energies. The slopes of the fitted lines in the lin-log plots give the corresponding total fragmentation cross sections.

**Figure 2.3:** Schematic of the the cluster aggregation source. An oven is mounted inside a container filled with He buffer gas at a pressure of about 1 mbar. Liquid nitrogen is used to cool the He gas to temperatures below 100 K such that weakly bound clusters may be formed.

### 2.2 Ion-impact induced fragmentation and molecular growth in molecular clusters

The experimental setup for high center of mass energy (> 10 keV) collisions is located at the ARIBE facility in Caen, France [4, 16]. There, keV ion beams
are produced in an Electron Cyclotron Resonance (ECR) ion source \[42, 75\] and guided to interact with a beam of neutral molecules or molecular clusters inside the extraction region of a linear time-of-flight mass spectrometer.

The neutral targets are produced in electrically heated ovens loaded with commercially available molecular powders. There are separate ovens for producing neutral monomer and cluster beams. When the monomer oven is heated, the molecules are evaporated and effuse into the interaction region through the oven exit hole. The cluster source oven has a similar design as the monomer oven but it is mounted inside a container filled with helium buffer gas where the pressure is of the order of millibars (see Figure 2.3). The molecules effuse from the oven and enter the condensation region where the helium gas is cooled down by liquid nitrogen to temperatures below 100 K. This leads to formation of weakly bound neutral clusters with a broad (lognormal) size distribution \[28, 30\]. The clusters are guided to the interaction region. The cluster size distribution depends on the oven temperature, increasing the temperature (number density) gives larger clusters. The temperature depends on the molecular species, e.g. 60 °C and 250 °C is typically set for producing anthracene and coronene monomers, respectively. Production of clusters often require higher temperatures.

Figure 2.4: Schematic of the time-of-flight mass spectrometer. A pulsed ion beam enters the interaction region of the spectrometer. The charged collision products are extracted and accelerated along the spectrometer axis shortly after the beam pulse has left the interaction region. The ions hit a metal plate at the end of the spectrometer. This produces secondary electrons which are guided by a weak magnetic field towards a MCP detector.

A schematic of the mass spectrometry setup is shown in Figure 2.4. The ion beam is chopped into \(\sim 1\mu s\) long pulses before entering the interaction region with a monomer or a cluster target. After the beam pulse has left the
interaction region, the charged collision products (intact and fragment ions) are extracted by a pulsed homogeneous electric field. The ions are then accelerated and enter a field free drift region. The acceleration system and the length of the drift region are designed to let ions with the same mass to charge ratio arrive at the same time at the end of the drift region regardless where they were produced in the interaction region. After the drift free region, the ions are further accelerated to increase the yield of secondary electrons emitted when they hit the metal plate at the end of the spectrometer. A weak magnetic field is then used to guide these electrons towards a MCP detector. The time difference between the start of the extraction pulse and a hit on the MCP detector gives the ion flight time. The metal plate combined with the weak magnetic field and the MCP system gives a high detection efficiency, which allows for detection of several charged fragments per collision event (coincidence measurements).
3. Theoretical tools and models

This section describes the theoretical tools and models which have been used to guide the interpretations of the experimental results. In Section 3.1 we present a model for energy transfer processes when ions and atoms penetrate the molecular electron clouds and interact with the individual nuclei in molecules or molecular clusters. In this model, we use a Monte Carlo technique where we calculate such electronic and nuclear stopping processes for random ion/atom trajectories through or close to the molecules or clusters. By performing a large set of trajectories we get information about the energy transfer distributions. The collisional energy transfer is typically statistically redistributed across all degrees of freedom before the system cool down by emission of photons, electrons, atoms, or molecules. However, prompt (non-statistical) atom knockout processes may also be important under certain circumstances (in low energy collisions with isolated molecules or high energy collisions with clusters).

In Section 3.2 we describe the molecular structure calculations which was used to investigate how the molecules and clusters respond to energy transfer processes. These calculations give information about e.g. the lowest dissociation energy pathways and reaction barriers for the intact molecules and the reactivity of fragments from non-statistical fragmentation. They were also used to produce collision model input parameters (nuclear coordinates and electron densities).

3.1 Collision model

3.1.1 Nuclear stopping

Nuclear stopping, i.e. when the projectile lose some of its kinetic energy by scattering on individual nuclei in the molecule, is the dominant energy loss mechanism for low collision energies (see Figure 1.4). In a classical picture, the energy lost by projectile atom with mass \( M_1 \), atomic number \( Z_1 \) and a target atom (\( M_2, Z_2 \)), is

\[
T_{\text{nuc}} = T_{\max} \sin^2 \frac{\phi}{2}
\]  

(3.1)
where
\[ T_{\text{max}} = \frac{4M_1M_2}{(M_1 + M_2)^2} E \] (3.2)
is the maximum energy transfer in head-on collisions and \( E \) is kinetic energy of projectile in laboratory system. The scattering angle in the center of mass system \( \phi \) (see Figure 3.1) is related to the impact parameter \( p \) by [80]:
\[
\sin \frac{\phi}{2} = \cos \left\{ \int_{r_{\text{min}}}^{\infty} \frac{pdr}{r^2 \sqrt{1 - \frac{V(r)}{E_{\text{CM}}} - \left( \frac{p}{r} \right)^2}} \right\} \tag{3.3}
\]
where \( E_{\text{CM}} \) is the center of mass collision energy, \( r_{\text{min}} \) is the closest distance between the projectile and target atom during the collision. This distance of closest approach can be found by solving the following equation
\[
1 - \frac{V(r_{\text{min}})}{E_{\text{CM}}} - \left( \frac{p}{r_{\text{min}}} \right)^2 = 0 \tag{3.4}
\]

**Figure 3.1:** Schematic showing the relation between the impact parameter (\( p \)) and the scattering angle (\( \phi \)) in the center of mass (CoM) energy system for the collision between two atoms (\( M_1 \) and \( M_2 \)).
where $V(r)$ is the interaction potential. In the present work, we use a Coulomb potential multiplied by different types of screening functions, $f(x)$,

$$V(r) = \frac{Z_1 Z_2}{r} f(x)$$

(3.5)

Lindhard [39] introduced screening function of the type

$$f_{\text{Lindhard}}(x) = \frac{k_s}{s} x^{1-s}$$

(3.6)

where $s$ is an integer and $k_s$ a constant determined by $s$. The variable $x$ is the ratio between the radial distance and the screening length ($a_{\text{Lindhard}}$)

$$x = \frac{r}{a_{\text{Lindhard}}} = \frac{r \sqrt{Z_1^{2/3} + Z_2^{2/3}}}{0.8853 a_0}$$

(3.7)

where $a_0$ is the Bohr radius. Lindhard applied an approximate method to evaluate $\phi$ (Eq. 3.3) and arrived at the following expression for $s=2$ and $k_2=0.831$

$$\sin^2 \frac{\phi}{2} = \frac{\pi p_0^2}{\pi p_0^2 + \pi p^2}$$

(3.8)

The corresponding analytical solution is (see Paper V)

$$\sin^2 \frac{\phi}{2} = \cos \frac{\pi p}{2\sqrt{p^2 + p_0^2}}$$

(3.9)

where

$$p_0^2 = \frac{0.831 Z_1 Z_2 a_{\text{Lindhard}}}{2E_{\text{CM}}}$$

(3.10)

The present analytical solution (Eq. 3.9) and the approximate solution (Eq. 3.8) give results in close agreement with each other. This is illustrated in the left panel of Figure 3.2 which shows a comparison between the two expressions for 100 eV collisions ($E_{\text{CM}}=100$ eV) between hydrogen ($Z_1=1$) and carbon ($Z_2=6$). In the right panel of Fig. 3.2 we show a comparison between the analytical expression for the Lindhard potential (Eq. 3.9) and the corresponding numerical results for the so called ZBL (Ziegler-Biersack-Littmark) potential [80]. The latter is commonly used for ions or atoms interacting with solids. The ZBL screening function is

$$f_{\text{ZBL}}(x) = 0.1818 e^{-3.2x} + 0.5099 e^{-0.9423x} + 0.2802 e^{-0.4029x} + 0.02817 e^{-0.2016x}$$

(3.11)
Figure 3.2: Comparison between Lindhard approximate expression and the present analytical solution for the scattering angle \( \phi \) as a function of impact parameter (left), and comparison between scattering angles obtained with the Lindhard (analytical solution) and the ZBL (numerical evaluation) potentials as a function of impact parameter for collision between hydrogen and carbon \((E_{CM} = 100 \text{ eV})\) (right). The insets show the ratios between the two curves.

where

\[
x = \frac{r}{a_{ZBL}} = \frac{r(Z_{0.23}^{1} + Z_{0.23}^{2})}{0.8853a_{0}}
\]

and \( a_{ZBL} \) is the ZBL screening length. We find that the ZBL and Lindhard potentials give rather similar results for light atoms (e.g. H or He) interacting with hydrogen or carbon atoms in the 100 eV collisions energy range (see the right panel of Figure 3.2). This allows us to use the analytical solution (Eq. 3.9) for the relation between the impact parameter \( p \) and the scattering angle \( \phi \) to get an analytical formula for single atom knockout out cross section per atom in the molecule

\[
\sigma = \pi p^2 = \frac{4\pi p_0^2}{\pi^2 \arccos^2\left(\frac{\sqrt{E_{th}/T_{\text{max}}}}{4}\right)}
\]

where \( E_{th} \) is the threshold energy for knockout. Here, we use the results from molecular dynamics simulations which show that the threshold energies for knocking out a carbon or a hydrogen atom from a PAH molecule are close to 27 eV and 9 eV, respectively (see Paper V for details). In Figure 3.3, we show the calculated cross sections for exceeding the thresholds for carbon knockout \((E_{th}^C=27 \text{ eV})\) in H+C, He+C collisions and hydrogen knockout \((E_{th}^H=9\text{eV})\) in H+H and He+H collisions.
3.1.2 Electronic stopping

The electronic excitation energies due to interactions with the PAH molecular electron clouds are calculated by treating the valence electrons (all electrons except the C 1s electrons) as a free electron gas. The energy lost by ion/atoms traversing an electron gas depends on the electron density distribution along the ion trajectories [21]. Here we assume that the electronic energy loss $T_e$ is proportional to projectile velocity [70] and the electronic stopping power is then given by

$$S = \frac{dT_e}{dR} = \gamma(r_s)v$$  \hspace{1cm} (3.14)

where $\gamma(r_s)$ is the so called friction coefficient, which is a function of the one-electron radius $r_s$

$$r_s = \left(\frac{3}{4\pi n_0}\right)^{\frac{1}{3}}$$  \hspace{1cm} (3.15)

where $n_0$ is the valence electron density. The electron density is inhomogeneously distributed within the molecules and is calculated by means of molecular structure calculations (see Section 3.2). The friction coefficient is related to the scattering phase shifts ($\delta_l$) through

$$\gamma(r_s) = \frac{3}{k_F r_s^3} \sum_{l=0}^{\infty} (l+1) \sin^2(\delta_l - \delta_{l+1})$$  \hspace{1cm} (3.16)
where \( k_F \) is the magnitude of the Fermi wave vector. The friction coefficients for various atoms and a few \( r_s \)-values have been calculated by Puska and Nieminen [55]. We fit exponential functions to their results (see the examples in Figure 3.4) to calculate the friction coefficients for any \( r_s \)-value.

In the simulations, we calculate the electronic stopping power (Eq. 3.15) for each point along random atom trajectories through the PAH molecular electron clouds. The stopping energy is then given by the stopping power multiplied by the step size. Simultaneously, we calculate the nuclear stopping energy as described in the preceding section. For each individual atom trajectory, the sum of these two contributions gives the model total stopping energy.

\[
\gamma(r_s) = \alpha_0 e^{-\beta r_s}
\]

where \( \alpha_0 \) and \( \beta \) are parameters determined from fitting to the data of Puska and Nieminen.

**Figure 3.4:** The friction coefficient for hydrogen and helium as a function of density parameter \( r_s \). The solid curves are exponential fitting functions, and the red squares are data from Puska and Nieminen [55].

### 3.2 Molecular structure calculations

Molecular structures calculations are carried out using the Gaussian09 package [23]. These give information about the dissociation energies and reaction barriers for the most important decay pathways, the coordinates of the optimized molecules (input for the nuclear stopping model), and the valence electron densities (input for the electronic stopping model).

In a typical calculation, the structure is optimized and the vibrational frequencies are then calculated. The latter is done to include the zero-point vibrational energy and to verify that the structure corresponds to a minimum.
on the potential energy surface (all frequencies are real) or a transition state (one imaginary frequencies). In these calculations, we have mainly used Density Functional Theory (B3LYP functional) and the 6-311++G(2d,p) basis set [3, 37]. We have also used the computationally more demanding Complete Basis Set (CBS-QB3) method [48, 49] for computing more accurate energies (paper VI).
4. Results & Discussion

In Section 4.1, we will discuss the results on PAH- and fullerene-monomer fragmentation in collisions with ions or atoms at low (about 100 eV) and high (several keV) center of mass collision energies. In Section 4.2, we will discuss results on molecular growth in clusters of PAHs and fullerenes.

4.1 Collisions with isolated PAH or fullerene molecules

4.1.1 Statistical fragmentation

Figure 4.1 shows the time-of-flight mass spectrum for collisions between 11.25 keV He$^+$ ions and coronene. The two highest peaks in the spectrum correspond to intact singly and doubly charged coronene. These are associated with rather low collisional energy transfers such that the intact, singly or doubly ionized molecule does not fragment on the experimental timescale of microseconds. The highest peak in the spectrum is attributed to single electron capture processes in large impact parameter collisions well outside the molecule (see the picture to the upper left in Fig. 4.1). The so formed singly charged coronene molecules are then produced cold enough to survive further fragmentation. The second highest peak is most likely due to somewhat closer non-penetrating ion-coronene collisions leading to capture of two electrons or to delayed thermionic emission processes [1] following single-electron capture. To the far left in the spectrum there are peaks representing small hydrocarbon fragments due to statistical fragmentation of coronene molecules which have been more strongly heated in collisions where the ion trajectories pass directly through the molecules (penetrating collisions). The insets in Fig. 4.1 show the regions for losses of one or several ($n$) hydrogen atoms from intact singly and doubly charged coronene. It can be seen clearly in Fig. 4.1 that even numbers of H-losses are highly preferred, which is similar to what has been observed earlier for PAH-fragmentation in collision with photons [43], electrons [17] and keV ions [15, 36].

The $n$H-loss peaks must be associated with comparatively low internal energies such that the remaining large PAH fragments, [PAH$^+$ - $n$H] remain sufficiently cold to survive the extraction phase in the time-of-flight spectrometer (microsecond timescale). By analysis of simple mass spectra alone it is im-
**Figure 4.1:** Mass-to-charge spectra for collisions between 11.25 keV He$^+$ and coronene (C$_{24}$H$_{12}$). The two highest peaks correspond to singly and doubly ionized coronene without fragmentation on the experimental timescale of about ten microseconds. The right and the left insets show the intensity distributions for losses of different numbers, $n$, of H-atoms from the coronene cat- and dications. Other peaks are due to fragmentation of the carbon-skeleton. The inset to the upper left shows the outer bound for one electron transfer from coronene to 11.25 keV He$^+$ (blue surface) according to the classical over-the-barrier model by Forsberg et al [22]. The outer bound for ion trajectories transferring at least 5 eV to the electron cloud of coronene is shown as a red surface.
possible to unambiguously determine whether the loss of two hydrogen atoms are due to $\text{H}_2$ emission or sequential H-emissions (H+H). To investigate this further, the dissociation energies, barriers and energy transfers to the PAHs in the collisions are required (see below).

<table>
<thead>
<tr>
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<th>1+</th>
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<tbody>
<tr>
<td>$\text{H}$</td>
<td>4.79</td>
<td>4.72</td>
</tr>
<tr>
<td>$\text{H}_2$</td>
<td>4.19</td>
<td>4.17</td>
</tr>
<tr>
<td>$\text{H}+\text{H}$</td>
<td>8.68</td>
<td>8.66</td>
</tr>
</tbody>
</table>

**Reaction barriers**

<table>
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<tr>
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<th>1+</th>
<th>2+</th>
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<tbody>
<tr>
<td>$\text{H}_2$</td>
<td>5.04</td>
<td>4.95</td>
</tr>
</tbody>
</table>

Units: eV

*Figure 4.2:* The lowest adiabatic dissociation energies and reaction barriers for emission of $\text{H}$, $\text{H}+\text{H}$ and $\text{H}_2$ molecules from singly and doubly charged coronene. The red circle represents the lowest dissociation energy channel, while the blue circle indicates the initial positions of two hydrogen atoms that connect to the lowest dissociation energy channels for (H+H)- and $\text{H}_2$. It is thus energetically favourable to emit $\text{H}_2$ from the same ring. It is also necessary to consider transition states and barriers when discussing the competition between $\text{H}_2$-loss and the loss of single H-atoms (see text).

The DFT (B3LYP/6-311++G(2d,p)) calculation results for the lowest adiabatic dissociation energies and reaction barriers for $\text{H}$, $\text{H}+\text{H}$ and $\text{H}_2$-losses from singly and doubly charged coronene are shown in Figure 4.2. The lowest dissociation energies correspond to emission of $\text{H}_2$ (∼4 eV), followed by emission of $\text{H}$ (∼5 eV) and $\text{H}+\text{H}$ (∼9 eV). For $\text{H}_2$ or $\text{H}+\text{H}$ emission it is energetically favourable when both hydrogen atoms are from the same ring. This seems to suggest that $\text{H}_2$-emission could be a dominant decay channel even for modest internal excitation energies. However, the $\text{H}_2$-emission pathway involves several transition states (see paper VI). The $\text{H}$- and (H+H)-emissions, on the other hand, do not involve any barriers. As shown in Fig. 4.2, the lowest barrier for $\text{H}_2$-emission is comparable with the energy required for single hydrogen dissociation. Therefore, these two processes could be competing in different ways for different internal energies. Figure 4.3 shows that the dissociation energies and reaction barriers are rather independent of PAH size and
Figure 4.3: The dissociation energies and reaction barriers for singly (left panel) and doubly (right panel) charged PAHs.
charge state.

Figure 4.4: The model (see Paper V) results of the energy and temperature distributions for various collision systems.

Figure 4.4 shows calculated energy and temperature differential cross sections for different collision systems at different collision energies. We have performed calculations for four different PAH targets and in each case we have launched large numbers (200000) of ion trajectories with random orientations of the molecules. In the left panels of Fig. 4.4 the energy distributions cover the 5-100 eV range. For collisions with 11.25 keV He\(^+\) there is a distinct peak at about 40 eV in all cases, which is due to the interaction between He and carbon-carbon bonds in the PAH molecule (see Paper V). In the right panels of Fig. 4.4 we have converted the horizontal axis to a temperature scale through \(E = (3N - 6)k_B T + E_d/2\), where \(N\) is the number of atoms in the molecule, \(k_B\) is the Boltzmann constant, and \(E_d=5\) eV is the dissociation energy of the PAH molecule. As it has been shown in Paper VI, the temperature at which significant H\(_2\) could be emitted is about 2200 K (see paper VI for more details). Clearly, most collisions yield internal temperatures exceeding that, suggesting that H\(_2\) indeed may be efficiently formed in the present keV-ion collisions. This also means that the remaining large fragments ([PAH-2H]\(^+\)) have high internal energies. Therefore it is likely that they fragment further and that the
2H-loss peak in the mass spectrum does not directly reflect the importance of H₂-loss even in cases where H₂ is likely to be produced.

4.1.2 Competition between statistical and non-statistical fragmentation

In Figure 4.5, we show the mass spectra due to C₁₄H₁₀⁺ + He and He⁺ + C₁₄H₁₀ collisions at center of mass energies of 110 eV and 11 keV, respectively. Results from Monte Carlo simulations of electronic and nuclear stopping processes are shown in the insets for the particular cases when the trajectories are perpendicular to the molecular planes. Electronic stopping processes dominate the energy transfer to the molecule at the higher collision energy (see the upper panel in Figure 4.5). Typical total internal energies are around 40 eV, which is well above the lowest dissociation energies of about 5 eV for H- or C₂H₂-loss. Many collisions will lead to statistical fragmentation processes in the 11 keV case [17, 36]. This is consistent with the distribution of fragments in the mass spectrum shown in the upper panel of Figure 4.5. The highest peak is due to intact C₁₄H₁₀⁺ at a mass-to-charge ratio of 178. The smaller peaks to the left are due to moderately heated systems which lose H- atom(s) and/or C₂H₂ molecule(s). The lighter fragments in the spectrum are due to more violent collisions where large amounts of energy are transferred (see Paper V for details).

The fragment mass spectrum is different in the 110 eV case. Here the nuclear stopping dominates as can be seen in the inset. According to the molecular dynamic simulations by Postma et al. [54], only nuclear stopping above about 27 eV will lead to prompt carbon knockout while 9 eV is sufficient for knocking out of a H-atom (see Paper V for details). Our calculations show that there are many collisions which lead to nuclear energy transfers above these thresholds at 110 eV. On the average the masses of fragments are larger here than in the cases of the higher energy collisions reflecting cooler anthracene molecules and fragments in the 110 eV case. The single carbon atom loss is important at 110 eV which is a clear signature of a non-statistical fragmentation process. As shown in Paper V, the much higher dissociation energies for C- or CHₓ-loss in relation to those for C₂H₂- or H- loss makes this channel insignificant for statistical fragmentation processes.

The calculated non-statistical, statistical and total (statistical + non-statistical) fragmentation cross sections using the ZBL potential and the total experimental cross sections for collisions between PAH cations and helium atoms with center of mass energy 110 eV are shown in Figure 4.6. Martin et al [40] measured the internal energies of fragmenting anthracene cations and found that about 10 eV is needed for statistical fragmentation on microsecond timescales,
Figure 4.5: Fragmentation mass-to-charge spectra for He + C\textsubscript{14}H\textsubscript{10} collisions at 11 keV (upper panel) and for C\textsubscript{14}H\textsuperscript{+}\textsubscript{10} + He at 110 eV center-of-mass energy collisions (lower panel). Insets show electronic and nuclear stopping contributions to the molecular excitation energies.
which is relevant for their and the present experiments. These results are used to calculate the total fragmentation cross section by assuming that trajectories associated with larger stopping energies (electronic plus nuclear) than 10 eV will lead to fragmentation of anthracene within microseconds. A subset of these trajectories will lead to much larger nuclear energy transfers to individual atoms in anthracene and lead to single-carbon knockout i.e. to non-statistical fragmentation. The threshold energy for statistical fragmentation should scale roughly with the number of atoms, \( N \), in the PAH

\[
T_{th}^{stat}(N) = \frac{3N - 6}{3 \times 24 - 6} \times 10 \text{ eV}
\]  

(4.1)

Here, the value 10 eV is the internal energy needed for fragmentation of anthracene, \( \text{C}_{14}\text{H}_{10} \), on the microsecond timescale. This has been measured directly by Martin et al [41]. In eq. (4.1) we scale this result with the number of degrees of freedom for an arbitrary PAH molecule containing \( N \) atoms. For anthracene \( N = 24 \). The scaling relies on the fact that dissociation energies are similar for PAHs of different sizes. This was shown to be the case for a range of PAHs by Holm et al [27].

We find that the model and experimental total fragmentation cross sections are similar for the PAHs considered here. We see from Figure 4.6 that the non-statistical knockout cross section becomes more important for larger PAHs and dominant for circumcoronene. The reason is that the statistical threshold energy \( T_{th}^{stat} \) increases as a function of PAH size, while the non-statistical threshold energy essentially is size independent - the chemical bonds within the PAH molecules have similar strengths for different PAH sizes.

From Figure 4.6, we see that the total cross sections are measured to be significantly smaller than the geometrical cross sections. This means that the PAHs are partially transparent to helium atoms with energies in the range around 100 eV.

In Figure 4.7, we show fragmentation spectra for 9 keV \( \text{C}_{60}^+ \) colliding with He, Ne, Ar and Xe yielding center of mass energies of 50 eV, 245 eV, 473 eV and 1388 eV, respectively. For the Ne, Ar and Xe targets we detect \( \text{C}_{59}^+ \) ions most likely stemming from prompt carbon knockout processes. In the case of the He target it was not possible to separate a possible corresponding contribution from features due to other processes. The He atom could be either scattered or captured to form endohedral He@\( \text{C}_{60} \) [11, 60, 73]. The scattering process gives a broad shoulder on the low-energy side of the primary beam peak. This shoulder extends to energy losses of about 200 eV, which corresponds to elastic scattering of He in the forward direction (see Paper III for details). Interestingly, the single carbon loss peaks are much smaller for \( \text{C}_{60} \) (Figure 4.7) than for PAHs (lower panel of Figure 4.5). A reason for this could
Figure 4.6: Statistical, non-statistical, and total fragmentation cross sections as calculated using the ZBL potential for PAH-cations colliding with He at 110 eV center of mass energy. Inset: Estimate of the geometrical cross section area of a coronene molecule $\sigma = 0.8 \pi d^2$, where the factor 0.8 is due to the random orientation of the molecule in the collision [22].
be that PAHs are planar while fullerenes have truly three dimensional molecular structures.

**Figure 4.7:** Fragmentation spectra for 9 keV $C_{60}^+$ (energy in the laboratory frame of reference) in collisions with He, Ne, Ar and Xe. There are more fragments for the heavier atoms where the center-of-mass energies are higher. The He may be inserted in the fullerene cage to form endohedral He@C$_{60}$ or scattered. Both processes contributes to the shoulder to the left of the main peak. Inset: A zoom-in with the expected C$_{59}^+$ position indicated.

### 4.2 Collisions with clusters of PAH or fullerene molecules

We show a mass spectrum for 22.5 keV He$^{2+}$ colliding with loosely bound van der Waals clusters of C$_{60}$ fullerenes in **Figure 4.8**. The total time-of-flight spectrum, where C$_{60}^+$ dominates is shown in the top panel of **Figure 4.8**. The low-intensity peaks to the right of C$_{60}^+$ are mainly due to intact [C$_{60}$]$_n$ ions (the intensity scales are different for the right and left panels of **Figure 4.8**). The peaks close to $n_C/e = 120$, where $n_C$ is the number of carbon atoms in the fragment, are shown in an expanded scale in **Figure 4.9** (first from left) with positions corresponding to $n_C/e=119$ and 118 etcetera. In the left top panel of **Figure 4.8** there are a few rather weak peaks due to the emission of one and
several $C_2$ molecules from $C_{60}$ monomer cations that have been left sufficiently hot to fragment. This could occur after several steps of fragmentation of a charged $[C_{60}]_n$-cluster leaving at the end one or several singly charged $C_{60}$ molecules of which a few may fragment further.

We show single stop events, i.e. events where only one charged fragment is detected, in the middle panel of Figure 4.8. The peaks in this panel are attributed to the most distant electron transfer collisions where the clusters become singly and doubly ionized. Here, only low amounts of energies are transferred to the individual molecules and the fragmentation is weak.

In the lowest panels in Figure 4.8 we show product ions measured in coincidence with $C_{60}^+$ ions. These events are mainly due to closer collisions and multiple ionizations of $[C_{60}]_n$-clusters in which substantial amounts of energy are transferred. A zoom-in on the peak in the lower right panel of Figure 4.9 reveals that there are peaks at $n_{C/e} = 118, 119$ and 120. The latter, could be due to weakly bound $[C_{60}]_2^+$ dimers from decays of larger clusters but may also be due to $C_{60}^+ + C_{60} \rightarrow C_{120}^+$ covalent bond formation. As there are substantial barriers involved in the formation of $C_{120}$ from two unperturbed $C_{60}$ molecules it could be reasonable to assume that this peak instead could be due to reactions where one of the $C_{60}$ cages are damaged. This could be caused by an incomplete knockout process where the C-atom does not actually leave the fullerene. The peaks at $n_{C/e} = 119$ and $n_{C/e} = 118$ are most likely produced in at low energy $C_{59}^+/C_{58}^+ + C_{60}$ reactions, in which covalently bound $C_{119}$ and $C_{118}^+$ dumb-bell systems are formed as discussed in detail in Papers I and II.

### 4.2.1 Molecular growth

We show a zoom-in of the mass region around $n_{C/e}=120$ in the spectrum due to $Ar^{2+} + [C_{60}]_n$ collisions in Figure 4.9. There are more peaks than in $He^{2+}$ case. We have performed electronic and nuclear stopping calculations for 22.5 keV $He^{2+}$ and 12 keV $Ar^{2+}$ collisions on both fullerene monomers and clusters. Highly reactive products (e.g. $C_{59}^+$, $C_{58}^+$, etc) are produced by prompt knockout processes due to nuclear stopping processes for the collisions on monomers and on clusters. The $C_{59}$ and $C_{58}$ produced in knockout collisions with monomers inevitably also become strongly heated due to electronic stopping processes. They would therefore decay very quickly - on subpicosecond time scales if they were isolated. In the clusters however, the electronic excitations of those individual molecules that are directly penetrated in the collision may share its excitation energy with other (colder) molecules in the cluster. In this way, fragments like $C_{59}$ and $C_{58}$ may stay intact long enough in order to react with other (intact) molecules in the cluster (see inset in Figure 4.9, Paper I and II). The knockout cross sections calculated using the nuclear stopping
Figure 4.8: Mass to charge-spectra due to 22.5 keV He$^{2+}$ + [C$_{60}$]$_n$ collisions. From top to bottom we show the total mass spectrum (all events including single- and multiple-stop events), single-stop events (only one ion registered per collision), and coincidences with only intact C$_{60}^+$ ions (one or several). There are different intensity scales for the parts of the spectra shown in the right and left panels.
model with the screened Bohr potential (see Eq. 3.5 and 3.6 in Section 3.2) are displayed in Figure 4.9. The cross sections are calculated assuming that the threshold for knocking out a carbon from a $C_{60}$ molecule is about 15 eV (this was the value used for the analysis in Paper I. We have later found, however, that much larger energy transfers to the molecular system are needed to break all bonds of a C-atom in a fullerene). In the He$^{2+}$ case, single knockouts are more likely than knockouts of two different C atoms. The situation is the opposite in the case of Ar$^{2+}$ where the projectile does not need to come as close to an individual C atom in the molecule to knock it out as was the case with He$^{2+}$. This is most likely the reason for the more extensive distribution of peaks due to molecular fusion processes in the case of Ar$^{2+}$.

![Figure 4.9: Zoom-ins on mass-to-charge spectra due to 22.5 keV He$^{2+}$ + $[C_{60}]_n$ (left panel) and 12 keV Ar$^{2+}$ + $[C_{60}]_n$ collisions (middle panel). The curves show events recorded in coincidence with one or several C$^{+}_{60}$ ions. The peaks are due to bond forming reactions in which e.g. dumbbell shaped C$_{119}$ molecules may be formed (an example is shown in the inset in the left panel). The bond formation process is most likely initiated by prompt knockouts of one or several carbon atoms in a C$_{60}$ molecule. The right panel shows calculated absolute cross sections for producing C$_m$-fullerenes in direct knock-out processes.](image)

In Figure 4.10 we show a few examples of typical reactions leading to formations of new molecular structures when pyrene clusters are hit by 12 keV Ar$^{2+}$ projectiles. In all three examples, the reactions are between one pyrene fragment and one intact molecule according to our molecular dynamics simulations [20]. Within a few tens of femtoseconds, bonds are formed by the interacting fragment and an intact pyrene molecule. The top row shows the
Figure 4.10: Snapshots from molecular dynamics simulations of 12 keV Ar$^+$ [C$_{16}$H$_{10}$]$_9$ collisions (three different trajectories). The molecular growth processes are typically started by prompt atom knockouts or bond cleavages. The highly reactive fragments then form covalent bonds with neighbouring molecules in the clusters on the sub-picosecond timescales.
case where no atom has been knocked out, but instead a C-C bond has been spilt open by the projectile. The dangling C atoms react with a neighboring intact molecule before the system emits a C\textsubscript{2}H\textsubscript{2} molecule. The latter is typically one of the lowest energy decay pathways in PAH molecules, and here it results in a fused C\textsubscript{30}H\textsubscript{18} molecule at mass 378 amu. The second row shows the inclusion of a C-atom (from a knockout process), reaction with an intact pyrene molecule and formation of a C\textsubscript{17}H\textsubscript{10} which undergoes a few isomerization steps during the 1 ps simulation time. In the last row of Fig. 4.10, C\textsubscript{31}H\textsubscript{19} is formed when a CH group has been knocked out from one pyrene molecule which then forms bond with another molecule. A single bond is formed with a neighboring pyrene where one ring in the merged product closes into a pentagon.
5. Concluding remarks

In this work, fragmentation and molecular growth processes following collisions between fullerene/PAH molecules or clusters and atoms or atomic ions are presented. Experiments were performed with the aid of two complementary experimental setups for studies of collisions at high center of mass collision energies (> 10 keV) and for low center of mass collision energies (< 1 keV). The experimental results have been discussed in view of a collision model, molecular structure calculations, and molecular dynamics simulations.

We show that high energy (keV energies in the center-of-mass system) are dominated by heating of the molecular electron clouds (electronic stopping). The excess energy is then statistically distributed among all degrees of freedom before the molecules or molecular clusters cool down by emitting photons, electrons, atoms or molecules. The typical energy transfers are well above the dissociation energy thresholds, which lead to rich fragment mass spectra. Molecular structure calculations show that the dissociation energies are rather independent of PAH size for the energetically most favourable decay pathways. The dissociation energies for H-loss and H₂-loss are about 5 eV and 4 eV, respectively. However, there are reaction barriers for H₂ emission, which significantly reduce the decay rate. As a consequence, H₂-emission is only important for high internal PAH temperatures (> 2200 K). Such temperatures are typically reached in the present collisions with keV ions/atoms but not upon e.g. single UV-photon absorption.

Non-statistical fragmentation refer to the process, in which a single carbon atom is knocked out directly from the molecule in Rutherford like atom-atom scattering processes. The latter has been observed in experimental studies of collisions between PAH/fullerene molecules and atoms at low center of mass collision energies (< 1 keV). In general this yields more reactive fragments than statistical fragmentation processes. For non-statistical fragmentation, simple scaling laws for estimates of absolute fragmentation cross sections have been deduced.

For collision between keV ions and molecular clusters, prompt knockout processes play a key role in the formation of new molecules. The highly reactive fragments may then form covalent bonds with neighbouring molecules in the clusters. The experiments were carried out for collisions between various atomic ions and clusters of fullerenes or pyrene molecules (C₁₆H₁₀). In the
former case, exotic dumbbell shaped molecules (e.g. $C_{119}$) are formed, while broad size distributions with masses corresponding to $C_{16+m}H_x$ with $m=1-21$ may be formed with the PAH cluster target.

Isolated PAHs or fullerenes and their clusters are believed to be important in various astrophysical environments [68][69]. However, little is known about how they e.g. are formed, destroyed or how they react when they are intact or when they have been fragmented. It is also not known if molecular hydrogen, $H_2$, may form directly from internally hot native PAHs. One study presented in this thesis suggests that this may indeed be the case. More detailed information about these intriguing aspects are of great interest for the future. This may e.g. be obtained using the experimental setups at the novel DESIREE (Double ElectroStatic Ion Ring Experiment) facility at SU. Possible future experiments involve studies of molecular growth processes inside size selected clusters at the standalone beam line for low energy (<100 eV) collisions (see Section 4.2), and studies of charge and energy transfer processes between anions and cations of PAHs/fullerenes in DESIREE [61][67]. In the latter case, different ranges of initial internal ion temperatures may be selected by storing the ions for different times before the collisions. By storing for long times the ions will equilibrate thermally with the ring and its vacuum vessel which may be operated down to about 12 K. From a theoretical point of view, calculations of the $H_2$ rates from internally heated PAHs would help to gauge the significance of such processes in astrophysical environments.
Appendix: Additional publications

Peer-reviewed articles

1. **Ions interacting with planar aromatic molecules: Modeling electron transfer reactions**
   DOI: [10.1063/1.4790164](http://dx.doi.org/10.1063/1.4790164)

2. **Ions colliding with polycyclic aromatic hydrocarbon clusters**
   DOI: [10.1088/0031-8949/2013/T156/014062](http://dx.doi.org/10.1088/0031-8949/2013/T156/014062)

3. **First storage of ion beams in the Double Electrostatic Ion-Ring Experiment: DESIREE**
   DOI: [10.1063/1.4807702](http://dx.doi.org/10.1063/1.4807702)

4. **Formation dynamics of fullerene dimers \( C_{118}^+, \, C_{119}^+, \, \text{and} \, C_{120}^+ \)**
   DOI: [10.1103/PhysRevA.89.062708](http://dx.doi.org/10.1103/PhysRevA.89.062708)
5. **Ions colliding with mixed clusters of C\textsubscript{60} and coronene: Fragmentation and bond formation**

*Physical Review A, 90, 022713, (2014).*
 DOI: [10.1103/PhysRevA.90.022713](https://doi.org/10.1103/PhysRevA.90.022713)

6. **Fragmentation of anthracene C\textsubscript{14}H\textsubscript{10}, acridine C\textsubscript{13}H\textsubscript{9}N and phenazine C\textsubscript{12}H\textsubscript{8}N\textsubscript{2} ions in collisions with atoms**

*Physical Chemistry Chemical Physics, 16, 21980, (2014).*
 DOI: [10.1039/C4CP03293D](https://doi.org/10.1039/C4CP03293D)

**Peer-reviewed conference contributions**

1. **Bond formation in C\textsubscript{59}\textsuperscript{+}-C\textsubscript{60} collisions**

*Journal of Physics Conference Series, 488, 012028 (2014).*
 DOI: [10.1088/1742-6596/488/1/012028](https://doi.org/10.1088/1742-6596/488/1/012028)

2. **Modeling electron and energy transfer processes in collisions between ions and Polycyclic Aromatic Hydrocarbon molecules**

*Journal of Physics Conference Series, 488, 102015 (2014).*
 DOI: [10.1088/1742-6596/488/10/102015](https://doi.org/10.1088/1742-6596/488/10/102015)

3. **Commissioning of the DESIREE storage rings - a new facility for cold ion-ion collisions**
4. **First results from the Double ElectroStatic Ion-Ring ExpEriment, DESIREE**


DOI: [10.1088/1742-6596/488/9/092003](https://doi.org/10.1088/1742-6596/488/9/092003)

5. **DESIREE: Physics with cold stored ion beams**


DOI: [10.1051/epjconf/20158401004](https://doi.org/10.1051/epjconf/20158401004)
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