Non-statistical fragmentation of large molecules in collisions with atoms

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Abstract. Non-statistical fragmentation processes are important when Polycyclic Aromatic Hydrocarbon (PAH) molecules, fullerenes, or other large molecules collide with atoms at center-of-mass energies from a few tens to a few hundreds of eV. The typical result is the prompt, billiard-ball-like knockout of single atoms (CH\textsubscript{x}-loss). This is distinct from the well-known statistical fragmentation patterns of these molecules, which are dominated by H- and C\textsubscript{2}H\textsubscript{2}-loss for PAHs and C\textsubscript{2}-loss for fullerenes. We have explored the role of non-statistical fragmentation of PAHs and fullerenes in a series of experimental and theoretical studies. In general, the yield of non-statistical fragments depends sensitively on their stability against secondary statistical fragmentation following knockout.

The detection of the fullerenes C\textsubscript{60} and C\textsubscript{70} in the planetary nebula Tc 1 [1], and more recently in a variety of different interstellar environments [2], has brought renewed focus on the formation and destruction mechanisms of fullerenes and other large molecules under astrophysically relevant conditions. Dunk \textit{et al.} recently demonstrated a closed network growth mechanism through which fullerenes exposed to carbon vapor incorporate sequential C or C\textsubscript{2} units to form larger species [3]. They suggest that such a “bottom-up” mechanism may be important in the outflows of carbon stars or supernovae. Other groups have investigated “top-down” fullerene formation from graphene flakes [4], amorphous carbon clusters [5], and Polycyclic Aromatic Hydrocarbon (PAH) molecules [6, 7]. The possible connection between fullerenes and PAHs is especially interesting as PAHs are thought to be ubiquitous throughout the interstellar medium [8]. A strong indication for this is the observation of infrared emission bands at wavelengths associated with the vibrational modes of fused hexagonal benzene ring structures which are typical of PAH molecules.

One important destruction mechanism for both fullerenes and PAHs is collisions with fast atoms or ions, particularly H and He. Such collisions, with center-of-mass energies in the 10-1000 eV range, should be especially important when shockwaves from exploding supernovae pass through regions containing PAHs [9], or when solar winds [10, 11] penetrate atmospheres such as that of Titan. It was recently shown that non-statistical fragmentation - the direct, prompt (fs)
knockout of single C or H atoms - is the dominant mechanism for PAH destruction under these conditions [12]. The clearest experimental signature of this process is the detection of charged fragments in which a single carbon atom (perhaps accompanied by an H atom) has been lost from the parent molecule:

\[ C_nH^+_mHe \rightarrow C_{n-1}H^+_{m-x} + CH_x + He. \] (1)

Such single-carbon loss processes are highly disfavored in statistical fragmentation, in which internal excitation is distributed over all degrees of freedom and the channels with the lowest dissociation energy usually dominate strongly. For PAHs, H-, H$_2$- and C$_2$H$_2$-loss are typical statistical fragmentation channels, with dissociation energies around 5-7 eV [13]. The dissociation energy for removing a single C atom is much higher, around 11-17 eV [12], and this channel is usually strongly suppressed when PAHs are excited by photons [14, 15, 16, 17], electrons [18, 19] or in collisions with ions at several keV of energy or more [20, 21, 22, 23, 24]. Similarly, fullerenes typically decay via C$_2$-loss where the dissociation energy is close to 10 eV [25, 26]. However, in collisions with He atoms at center-of-mass energies around 100 eV, nuclear stopping processes - Rutherford-like scattering of the projectile ion or atom on individual (screened) atomic nuclei in the molecules - dominates. The energy transfer to these nuclei may then be sufficient to directly remove them, i.e. to knock them out, on sub-femtosecond timescales. In this scenario, fragmentation occurs before the energy is distributed over the internal degrees of freedom of the molecule.

For PAHs, single-carbon knockout frequently results in fragments containing pentagons that may lead to non-planar structures [12]. These are both key features of any hypothetical route to fullerene formation.

We have investigated the role of non-statistical fragmentation of PAHs and fullerenes in a series of experimental and theoretical studies. The main results of these works are reviewed here, and we provide preliminary results of ongoing projects.

Collision experiments are conducted in the Ion Source Lab, part of the DESIREE (Double ElectroStatic Ion Ring ExpErimentS) facility [27]. The experimental setup is shown in Figure 1. Molecular ions (both protonated and radical cation species) are produced in an electrospray ion source. A radio frequency (RF) ion funnel collects and focuses the ions into an octupole trap. This trap may be used as a pre-trap for loading a cryogenic ring electrode trap (RET), but for most of our experiments it is used in a continuous mode as an ion guide. A second octupole ion guide is used to transport the ions though a differential pumping stage. A quadrupole mass filter selects the ions of interest by their mass-to-charge ratio. A quadrupole deflector is used to direct the ions either to the RET, to an electron multiplier detector used to optimize ion source conditions, or to the acceleration stage. The ions are accelerated over a 1 - 10 kV potential difference applied across a stack of ring electrodes. A set of electrostatic deflectors and an Einzel lens (neither of which are shown in the schematic) are used to steer the beam into the opening of a 40 mm long gas cell. Due to the low laboratory velocity of the ions, the angular divergence of the beam after fragmentation can be significant. In order to ensure that all fragments leaving the gas cell are collected, a large-diameter electrostatic energy analyzer consisting of an Einzel lens and two sets of deflector plates has been developed to separate the fragment ions. The ions are detected using a microchannel plate (MCP) with a position sensitive resistive anode. Absolute total fragmentation cross sections are obtained by measuring the attenuation of the parent beam as a function of pressure in the gas cell. Recently, an electrostatic Cone Trap [28, 29] was installed at the end of the analysis beamline directly in front of the MCP. This new ion beam trap will be used to study the properties of fragments formed in the collisions.

In Figure 2 we show mass spectra for two PAH cations, anthracene C$_{14}$H$_{10}^+$ and coronene C$_{24}$H$_{12}^+$, following collisions with He at 110 eV center-of-mass energy. Both spectra are normalized to the height of the parent ion peak, which is off scale. Individual peaks due to
fragments with different numbers of H atoms are not resolved. The peak corresponding to the non-statistical loss of a single carbon atom is clearly visible in both cases but is much more prominent for coronene. The lower panel shows the relative intensity of the CH$_x$-loss peak as a function of mass for several PAHs, including anthracene (m/z=178 amu) and coronene (m/z=300 amu). Also shown is the relative intensity of the C$_2$H$_y$-loss peak, the main statistical fragmentation channel, which decreases with PAH size. These data show that non-statistical fragmentation becomes more important, and statistical fragmentation less important, for larger PAHs at a given center-of-mass energy (here 110 eV). This is because larger molecules have more degrees of freedom over which to distribute the energy deposited in the collision [12]. Thus the parent ion less likely to undergo statistical fragmentation on the experimental timescale (tens of microseconds), leading to reduced C$_2$H$_y$-loss. Similarly, the non-statistical C$_{n-1}$H$_{m-x}$+ fragments (Equation 1) are more likely to survive the experimental timescale, leading to an increase in this signal for larger PAHs.

This trend towards greater yields of non-statistical fragments for larger molecules does not hold for the fullerenes [30]. In Figure 3 we show mass spectra for C$_{60}^+$ cations colliding with He, Ne, Ar and Xe atoms (note the logarithmic intensity scale). These measurements were all performed with 9 keV acceleration energy. The center of mass energy thus varies from 50 eV for He to 1400 eV for Xe. For Ne, Ar and Xe, very small amounts of C$_{59}^+$ are formed by single carbon knockout. The yields are comparable to those obtained by other researchers in collision experiments with C$_{60}^-$ anions [31, 32]. For He, no signature of non-statistical fragmentation can be discerned due to the broad shoulder of the parent ion beam, which is due to scattering i.e. collisions which lead energy loss without fragmentation. The low yield of C$_{59}^+$ is likely a result of lower barriers to secondary statistical fragmentation than for the analogous PAH fragments. Additionally, the three dimensional structure of C$_{60}^+$ makes knockout of multiple carbon atoms more likely and leads to greater heating (and thus more statistical fragmentation) of the molecule.

In Figure 4 we give an example of how the yield of non-statistical fragments can change by changing the barriers to secondary statistical fragmentation. Here we show mass spectra for anthracene cations (C$_{14}$H$_{10}^+$), protonated acridine (C$_{13}$NH$_{10}^+$) and protonated phenazine (C$_{12}$N$_2$H$_{10}^+$) following collisions with noble gas atoms at 5 keV acceleration energy. These three molecules have similar structures, but acridine and phenazine have one or two carbon atoms replaced with nitrogen atoms. Such Polycyclic Aromatic Nitrogen Heterocycles (PANHs) have lower dissociation energies due to the relatively weak C-N bonds [33]. This leads to very different fragmentation patterns for the three molecules, even though their total fragmentation cross sections are very similar [34]. In particular, the $n=13$ peak, corresponding to knockout of a single heavy atom (C or N) and where n is the number of heavy atoms remaining in the charged fragment, decreases with each additional N atom in the parent ion for all target gasses.
This is attributed to the decreased survival probability of these non-statistical fragments owing to their lower dissociation energies. The relative intensity of the \( n = 13 \) peak also decreases with increasing mass of the target gas atom, as more energy is deposited into the molecule in collisions with heavier atoms.

We have also observed significant differences in the fragmentation patterns of isomeric PAHs following collisions with He at center-of-mass energies of 110 eV. This is in contrast to collision experiments in other energy regimes, where statistical processes (H- and C\(_2\)H\(_2\)-loss) dominate and the resulting mass spectra are nearly indistinguishable [35, 36, 37, 38]. We have performed a study of 12 PAHs from three isomeric sets: \( \text{C}_{16}\text{H}_{10}^+ \), \( \text{C}_{18}\text{H}_{12}^+ \) and \( \text{C}_{20}\text{H}_{12}^+ \). Peaks corresponding to different numbers of H atoms are not resolved and so the data are analyzed in terms of \( n \), the number of carbon atoms remaining in the charged fragment. In Figure 5 we show the absolute cross section for detecting \( \text{C}_n\text{H}_x \) fragments. This is simply the product of the integrated relative intensity of the \( \text{C}_n\text{H}_x \) fragment peak group and the absolute backbone fragmentation cross section measured by the beam attenuation method [34]. For the \( \text{C}_{16}\text{H}_{10}^+ \) isomers, we find large differences in the \( n = 15 \) cross sections. These fragments are due to single carbon knockout. Interestingly, the \( n = 14 \) and 13 peaks are nearly identical. The \( n = 3 - 10 \) peaks, which mainly represent multi-fragmentation channels, are also significantly different, with the trend in \( e.g. \) the \( n = 6 \) peak opposite to the one for \( n = 15 \). In contrast to the \( \text{C}_{16}\text{H}_{10}^+ \) case, the cross sections for the multi-fragmentation channels \( n < 12 \) for the \( \text{C}_{18}\text{H}_{12}^+ \) and \( \text{C}_{20}\text{H}_{12}^+ \) isomers show no significant variations, but variations in the higher-mass dissociation channels remain. The \( \text{C}_{18}\text{H}_{12}^+ \) isomers show small variations in the six highest mass peaks \( (n = 12 - 17) \) while the \( \text{C}_{20}\text{H}_{12}^+ \) isomers differ in the \( n = 16 - 19 \) peaks, with the greatest variation in the \( n = 19 \) single carbon loss peak. It is clear from these data that the structure of isomeric PAHs plays an important role in the survival probability of non-statistical fragments formed by single-carbon knockout.
Figure 4. Fragment mass distributions for anthracene cations, protonated acridine and protonated phenazine colliding with noble gas atoms. The number of heavy atoms (C or N) remaining in the molecule is \( n \). Structures of the neutral molecules (without protonation) are shown below.

Figure 5. Absolute cross sections for detecting fragments containing \( n \) carbon atoms following collisions between PAH\(^+\) cations and He atoms at 110 eV. Error bars due to the 5% uncertainty in the total fragmentation cross sections are smaller than the symbols. Molecular structures are shown in Figure 6.

Figure 6. Structures of PAH isomers investigated. Numbers refer to Figure 5.
The results discussed above have all highlighted the importance of the internal energy of the fragments formed by non-statistical single-carbon knockout processes. We now turn our attention to the role of the center-of-mass collision energy $E_{CM}$. Specifically, we wish to determine the minimum threshold energy for which single carbon knockout can be observed experimentally. In the left frame of Figure 7, we show several mass spectra for coronene $C_{24}H_{12}^+$ colliding with He at several different values of $E_{CM}$. The intensity of the single-carbon knockout peak decreases with $E_{CM}$ until it is almost indistinguishable from the background near the energy threshold.

The threshold behavior may be clearly seen in the right frame of Figure 7, where we plot the integrated relative intensity of the CH$_x$-loss peak as a function of $E_{CM}$ for three different PAH cations (anthracene $C_{14}H_{10}^+$, pyrene $C_{16}H_{10}^+$, and coronene $C_{24}H_{12}^+$) colliding with He. The integrated relative intensity is found simply by integrating the peak and dividing by the integral of all the fragments from which at least one C atom has been lost (fragments where only H atoms have been lost are not included). In addition to background subtraction, a correction is also applied to account for the fact that our energy analyzer is scanned at a constant rate, meaning that lighter fragments are swept across the detector faster than heavier fragments. The principle source of uncertainty in this procedure is the background subtraction at low energies, where there is also significant blending of the parent ion, CH$_x$-, and C$_2$H$_y$-loss peaks.

For the PAH ions in Figure 7, a rapid increase in the relative intensity of the CH$_x$-loss peak is observed between $E_{CM}=30$ and $50$ eV, above which a broad plateau is observed. The differing heights of the plateau regions reflect the size dependence of the survival probability discussed above (Figure 2). The value of the energy threshold (about $30$ eV) is in good agreement with that predicted by classical Molecular Dynamics simulations [39].

As with all studies of molecular fragmentation, it is important to consider the timescales involved. In our experiments, fragmentation must occur before the ions reach the electrostatic energy analyzer, approximately $10$ µs after collision. Non-statistical, single-carbon knockout is a prompt process which occurs on fs timescales, but secondary statistical fragmentation may occur on much longer timescales, particularly for large systems with many degrees of freedom. In order
Figure 8. Left: schematic of Cone Trap for storing fast ions. Right: decay curves showing emission from Cone Trap when anthracene cations (Ant\(^+\)) and [Ant-C\(_2\)H\(_2\)]\(^+\) fragments are stored.

to probe this and other long-timescale processes, we have designed and built a Cone Trap [28, 29], an electrostatic ion beam trap using two conical mirrors, shown schematically in Figure 8. The trap has been modified from the original design of Schmidt et al. [28], with larger openings in the ends of the mirrors to maximize throughput in mass spectroscopy experiments when the trap is not in use. We have performed preliminary experiments where we have successfully trapped and stored PAH ions as well as their fragments. For these experiments we have used a cryogenic Ring Electrode Trap (RET, see Figure 1) to create short, intense bunches of PAH cations, which were then accelerated to 3 keV and trapped in the Cone Trap. The emission of particles from the trap, assumed to be proportional to the population of stored ions, is monitored with a MCP detector. The main source of this emission is thought to be neutralization of stored ions in collisions with background gas. In Figure 8, we show the decay of the emission from stored beams of anthracene cations (Ant\(^+\), C\(_{14}\)H\(_{10}\)) as well fragment ions where one C\(_2\)H\(_2\) unit has been lost from the anthracene cation in collisions with He ([Ant-C\(_2\)H\(_2\)]\(^+\), C\(_{12}\)H\(_8\)\(^+\)). The decay rate of the emission is similar for the two stored ion beams, indicating that both species have similar neutralization cross sections. The decay of the Ant\(^+\) beam appears slightly non-exponential, which may be due to space charge effects or the result of Ant\(^+\) ions undergoing multiple collisions prior to neutralization. These measurements alone are not sufficient to probe two-step fragmentation processes, as the charged fragments formed in the trap are (according to SIMION simulation) most likely stored along with the parent ions. In the future we plan to couple the Cone Trap to a time-of-flight mass spectrometer such that the content of the trap, including stored secondary fragments formed in the trap, can be probed as a function of storage time.

We have explored several aspects of non-statistical fragmentation of PAHs and fullerenes in collisions with atoms. We find that single-carbon knockout is an important process for PAHs at center-of-mass collision energies above 30 eV and up to a few keV. The yield of non-statistical fragments depends sensitively on the internal energy of the fragment and the barriers it faces to secondary statistical fragmentation. For fullerenes, the signature of single-carbon knockout is much weaker. Further theoretical and experimental work, including measurement of the timescales required for secondary statistical fragmentation, is needed to further understand these processes.

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