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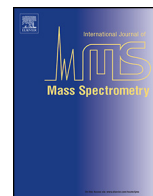
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Short communication

## Isomer effects in fragmentation of Polycyclic Aromatic Hydrocarbons



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### ABSTRACT

We have observed significant differences in the fragmentation patterns of isomeric Polycyclic Aromatic Hydrocarbon (PAH) cations following collisions with helium atoms at center-of-mass energies around 100 eV. This is in contrast to the situation at other collision energies or in photo-absorption experiments where isomeric effects are very weak and where the lowest-energy dissociation channels (H- and C<sub>2</sub>H<sub>2</sub>-loss) dominate in statistical fragmentation processes. In the 100 eV range, non-statistical fragmentation also competes and is uniquely linked to losses of single carbon atoms (CH<sub>x</sub>-losses). We find that such CH<sub>x</sub>-losses are correlated with the ionic ground state energy within a given group of isomers. We present results for three C<sub>16</sub>H<sub>10</sub><sup>+</sup>, four C<sub>18</sub>H<sub>12</sub><sup>+</sup> and five C<sub>20</sub>H<sub>12</sub><sup>+</sup> isomers colliding with He.

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### 1. Introduction

The relaxation and fragmentation mechanisms of Polycyclic Aromatic Hydrocarbons (PAHs) continue to draw the interest of researchers from a diverse range of disciplines such as astrophysics, atmospheric science and cancer research [1–3]. PAHs are common byproducts of combustion processes and are important components of soot and other forms of pollution [4,5]. Extensive observational evidence strongly suggests that PAHs are present in a wide range of astrophysical environments [6]. PAH molecules often contain fused hexagonal rings of carbon atoms and have hydrogen atoms on their outer rims. They may also have 4- or 5-membered rings or rings with more than 6 carbon atoms (see Table 1). For a given chemical formula C<sub>N</sub>H<sub>M</sub>, there are many structural PAH isomers which may have very different chemical properties. As an example, the solubility in water of two C<sub>14</sub>H<sub>10</sub> isomers, anthracene and phenanthrene, differ by more than a factor of 20 [7].

One important question is to what extent different PAH isomers fragment in different ways and with different rates in space. Based on their characteristic infrared emission features, it has

been suggested that PAHs in circumstellar regions associated with planetary nebulae have mainly large (>50 C atoms), compact structures whereas PAHs in the harsher environment of the interstellar medium (ISM) have irregular corrugated structures [8,9]. Possible reasons for this could be faster photo- and/or ion processing of PAHs in the ISM. Energetic (around 100 eV) collisions with hydrogen and helium atoms/ions in supernova shocks is thought to be an important pathway for interstellar PAH processing [10]. It has recently been shown that non-statistical fragmentation driven by prompt, single atom knockout may be the primary PAH destruction channel under these conditions [11–13]. Compared to statistical fragmentation, where stable low-energy products are favored, non-statistical knockout of single carbon atoms often leads to different, more highly reactive fragments [11,14,15]. One may ask whether such non-statistical fragmentation processes also may lead to enrichment of certain classes of isomers in, for example, the ISM.












The development of new techniques to discriminate between PAH isomers is an active area of mass spectrometry. Isomeric recognition and separation methods generally rely on chromatographic [16] or selective photo-ionization methods [17,18]. Several authors have reported isomeric sensitivity in the collision induced dissociation (CID) of [PAH+Ag]<sup>+</sup> complexes formed by electrospray ionization [19,20]. Some minor differences in the branching ratios between H- and C<sub>2</sub>H<sub>2</sub>-loss (the dominant dissociation channels for PAHs) have been observed following photo-absorption processes

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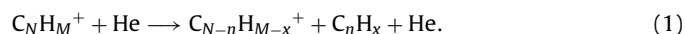
**Table 1**

Absolute fragmentation cross sections ( $10^{-15} \text{ cm}^2$ ) for PAH cation isomers in collisions with He atoms at 110 eV center-of-mass energy. Cross sections are given for losing at least one carbon atom ( $C_{n \geq 1}H_x$ -loss) and exactly one carbon atom ( $CH_x$ -loss). In the bottom row we give the ground state energies (GSEs, eV) relative to the most stable isomer, as calculated by density functional theory (see text).

| Isomer                     | $C_{16}H_{10}^+$      |   |   | $C_{18}H_{12}^+$  |   |   |   |
|----------------------------|-----------------------|---|---|---|---|---|---|
|                            |                       |  |  |  |    |  |  |
|                            | (1)<br>Pyrene         | (2)<br>Fluoranthene   | (3)<br>Benzo[b]biphenylene  | (4)<br>Chrysene   | (5)<br>Benz[a]anthracene  | (6)<br>Tetracene  | (7)<br>Triphenylene   |
| $\sigma_{C_{n \geq 1}H_x}$ | 2.0                   | 1.9   | 2.1   | 2.2   | 2.1   | 2.0   | 1.8   |
| $\sigma_{CH_x}$            | 0.24                  | 0.28  | 0.19  | 0.28  | 0.28  | 0.27  | 0.22  |
| GSE                        | 0.00                  | 1.02  | 2.48  | 0.22  | 0.12  | 0.00  | 0.54  |
| Isomer                     | $C_{20}H_{12}^+$      |   |   |   |   |   |   |
|                            |                       |  |  |  |  |  |   |
|                            | (8)<br>Benzo[e]pyrene | (9)<br>Benzo[a]pyrene   | (10)<br>Perylene  | (11)<br>Benzo[b]fluoranthene  | (12)<br>Benzo[k]fluoranthene  |   |   |
| $\sigma_{C_{n \geq 1}H_x}$ | 1.9                   | 2.2   | 2.1   | 2.1   | 2.2   |   |   |
| $\sigma_{CH_x}$            | 0.45                  | 0.44  | 0.40  | 0.36  | 0.34  |   |   |
| GSE                        | 0.23                  | 0.00  | 0.08  | 0.96  | 0.75  |   |   |

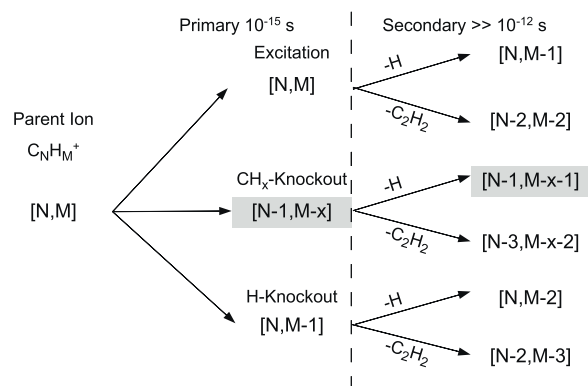
[21,22] or low-energy (1–10 eV) CID experiments where the PAH ions experience many collisions with the target gas in an ion trap [16,23,24]. However, the fragment mass spectra of PAH isomer have until now typically been found to be very similar following high-energy CID under single-collision conditions [25–28]. In relation to this it has been argued that, given the high stability of PAHs, there may be sufficient time for them to isomerize prior to dissociation such that the fragmentation pattern becomes insensitive to the original isomeric form. Indeed, isomerization barriers of some PAHs are rather close to their dissociation energies [29]. The non-statistical single atom knockout process, however, is prompt and occurs within femtoseconds which is much shorter than typical isomerization time scales [30,11,12].

In this work, we report significant isomeric differences in the fragment mass spectra following collisions between PAH<sup>+</sup> cations and He atoms at center-of-mass energies around 100 eV:



We present results for a total of 12 PAHs from three isomeric sets:  $C_{16}H_{10}^+$ ,  $C_{18}H_{12}^+$  and  $C_{20}H_{12}^+$ . Structures for the molecules are shown in Table 1. In all cases, we observe isomeric effects in product distributions following non-statistical fragmentation ( $n=1$  in Eq. (1)). For PAHs, the loss of an H atom or a  $C_2H_2$  molecule are the lowest-energy dissociation pathways, with dissociation energies of 5–7 eV [31]. These channels are indeed found to be the dominant statistical fragmentation channels when PAHs are excited by photons [21], electrons [32] or high-energy (>10 keV) ions [33]. Loss of a single C atom (or  $CH_x$ -loss) is associated with much higher dissociation energies (11–17 eV [11]) and high reaction barriers [34,35].

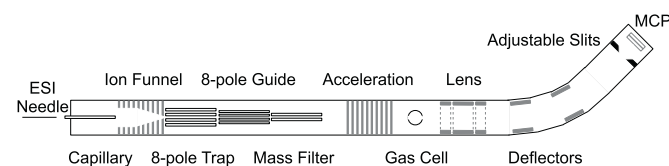
Following such an initial knockout process ( $CH_x$ -loss), sufficient energy may remain in the  $C_{N-1}H_{M-x}^+$  fragment for secondary, statistical fragmentation to occur within the present experimental timescale of some tens of microseconds. This secondary step may deplete the  $CH_x$ -loss peak if it involves the loss of additional carbon atoms, e.g.  $C_2H_2$ -loss, from  $C_{N-1}H_{M-x}^+$ . When the secondary step only includes H-loss(es), however, this does not affect the intensity of this peak. These decay pathways are illustrated in Fig. 1.



**Fig. 1.** Simplified diagram of the most important fragmentation channels for PAH cations  $C_N H_M^+$ . The numbers in brackets represent the number of C and H atoms remaining in the larger fragment on femtosecond time scales (left) and on time scales longer than picoseconds (right). Pathways resulting in the loss of a single carbon atom, the main signature of non-statistical fragmentation, are highlighted in grey. Following knockout it is possible that secondary (statistical) fragmentation occurs for example through emission of a  $C_2H_2$  unit from the  $C_{N-1}H_{M-x}^+$  fragment.

## 2. Materials and methods

Continuous PAH cation beams are produced by ElectroSpray Ionization (ESI). The electrospray ion source has been described previously [34] and is shown schematically together with beam steering equipment, the collision gas cell and the fragment analysis system in Fig. 2. Concentrated solutions of PAHs (Sigma–Aldrich) in dichloromethane, 0.5 mmol  $AgNO_3$  in methanol, and pure methanol are mixed in various proportions (depending on the



**Fig. 2.** Schematic of the electrospray ion source (ESI), collision cell and the electrostatic fragment analysis system with its position sensitive Microchannel Plate Detector (MCP).

solubility and ionization potential of the PAH) to achieve a stable spray and optimal ion beam intensity. A custom made ion funnel collects the ions. The octupole trap and guide are used simply to transport the beam through several stages of differential pumping. Great care was taken to ensure that all isomers were studied with the same ion source conditions. Following mass selection by the quadrupole mass filter, the ions are accelerated to 5.66–7.03 keV in the laboratory frame (110 eV in the PAH-He center-of-mass frame in all cases) and sent through a 4 cm long collision cell containing He gas. The kinetic energies of the resulting fragment ions are analyzed with two identical sets of electrostatic deflectors and a cylinder lens (the latter to reduce the angular divergence of the beam). The position of each ion impact on the 40 mm diameter microchannel plate (MCP) detector is recorded using a resistive anode. This information is combined with the deflector voltage and the known dispersion of the system to reconstruct the energy-per-charge (fragment mass-per-charge) spectrum. This method gives a high throughput, a mass resolving power of 30–50, and a high signal to noise ratio.

Absolute cross sections for the loss of at least one carbon atom were determined by measuring the attenuation of the various PAH isomer beams as functions of the He pressure in the gas cell [11]. For these measurements, we positioned the parent ion beam at one edge of the detector such that ions having lost one, two, three or four H atoms but no carbon atoms were collected on the detector together with the primary beam and did thus not contribute to the measured attenuation cross section. Fragments having lost one or more carbon atoms were not counted. This measurement thus yields the total carbon backbone fragmentation cross section, corresponding to Eq. (1) with  $n \geq 1$ . The statistical errors in these measurements are less than 5%.

### 3. Results and discussion

Mass spectra resulting from collisions between two isomers from each set and He are shown in Fig. 3. These spectra are normalized to the total integrated intensity of all fragments having lost at least one carbon atom. Individual peaks due to different hydrogenation states are not resolved due to the wide kinetic energy distribution of the fragments. The numbers of carbon atoms  $n$  lost from the fragment  $C_{N-n}H_{M-x}^+$  are indicated in the spectra. Significant differences in the intensities of the four highest-mass fragment peaks are obvious in each frame of Fig. 3. For example, the peak corresponding to single carbon knockout ( $n = 1$ ) is larger than the  $C_2H_2$ -loss peak ( $n = 2$ ) for benzo[e]pyrene (8), while for benzo[k]fluoranthene (12), the opposite is true.

In Table 1 we give our measured absolute carbon backbone fragmentation ( $C_{n \geq 1}H_x$ -loss) and single carbon knockout ( $CH_x$ -loss) cross sections for each PAH isomer. The  $CH_x$ -loss cross sections are the product of the  $C_{n \geq 1}H_x$ -loss cross sections and the integrated relative intensities of the  $CH_x$ -loss peak in the measured mass spectra, and thus represent the probability of detecting the  $C_{N-1}H_{M-x}^+$  fragments on the experimental time scale of tens of microseconds. While the  $C_{n \geq 1}H_x$ -loss cross sections are fairly similar within each set of isomers, the  $CH_x$ -loss cross sections vary significantly.

Also shown in Table 1 are the ground state energies (GSEs) of the singly charged parent molecules relative to that of the isomer with the lowest GSE (*i.e.* the highest binding energy). These values are calculated with Density Functional Theory (DFT) using the B3LYP functional and the 6-311G(d,p) basis set as implemented in the GAUSSIAN09 package [36]. In Fig. 4, we show correlations between the GSEs and the absolute  $CH_x$ -loss cross sections for the  $C_{16}H_{10}^+$ ,  $C_{18}H_{12}^+$ , and  $C_{20}H_{12}^+$  isomers. The energy cost for removing a single carbon atom depends mainly on the local binding environment [34] and not so much on the isomeric form. Thus, we may expect that the cross section for an initial carbon knockout process ( $CH_x$ -loss)

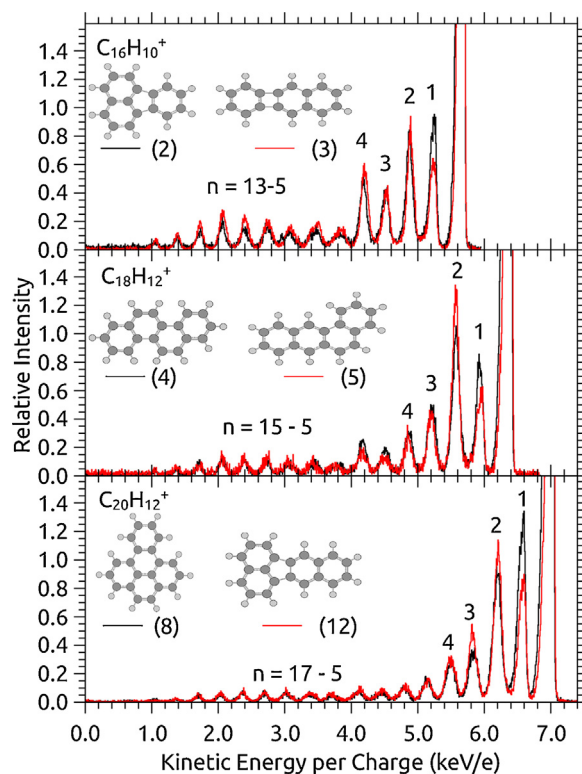


Fig. 3. Typical mass spectra for two  $C_N H_M^+$  isomers from each set following collisions with He at 110 eV. The number of carbon atoms  $n$  lost from the fragment  $C_{N-n}H_{M-x}^+$  is indicated for  $n = 1$  to  $N - 3$ . The numbers in parentheses, (2) etc., refer to the specific isomers in Table 1.

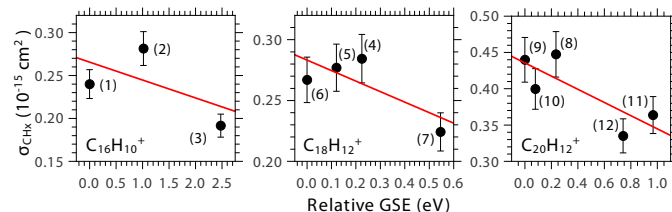


Fig. 4. Absolute  $CH_x$ -loss cross sections ( $\sigma_{CH_x}$  for  $C_{16}H_{10}^+$ ,  $C_{18}H_{12}^+$  and  $C_{20}H_{12}^+$  isomers versus the relative ground state energies (GSEs) of the parent ions. The numbers in parentheses, (1) etc., refer to the specific isomers in Table 1. Note the differences in horizontal scales between the three panels. The red lines are linear fits to guide the eye.

should be rather insensitive to the isomeric form. It is rather the differences in survival probabilities among the  $C_{N-1}H_{M-x}^+$  fragments that may explain the observed trends in Fig. 4. A more weakly bound isomer (*i.e.* one with a higher GSE) will, on the average, result in a more weakly bound product with a higher tendency for secondary decay processes of the types shown in Fig. 1.

### 4. Conclusion

We have observed significant differences in the fragmentation spectra of isomeric PAH cations following collisions with He atoms at center-of-mass energies of 110 eV. These differences are much greater than what is typically observed for pure statistical fragmentation processes [25–27] and are most likely linked to the competition between non-statistical and statistical fragmentation processes at the present collision energies. The present results suggest that the absolute cross sections for the loss of at least one carbon atom from different PAH isomers are nearly the same. However, the fragment distributions are different in that the more stable

isomers favor production of fragments having lost single carbon atoms. We have shown that there is a correlation between the ground state energy (GSE) of a PAH isomer and the single-carbon knockout ( $\text{CH}_x$ -loss) cross section. The lower the GSE (*i.e.* the higher the binding energy) of the isomer the larger the  $\text{CH}_x$ -loss cross section becomes within a given group of isomers. This is most likely due to differences in stabilities of the fragments left behind after single-carbon knockout. This is further evidence that single carbon loss is non-statistical and could be of importance for the chemistry in the cold interstellar medium (ISM) and may for example lead to enrichment of certain classes of PAH isomers. It will be interesting to investigate if these differences could be even stronger close to the threshold region of single-carbon knockout [34] and if these knockout thresholds are different for different PAH isomers.

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