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_2H_2-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_x-losses). We find that such CH_x-losses are correlated with the ionic ground state energy within a given group of isomers. We present results for three $C_{16}H_{10}^+$, four $C_{18}H_{12}^+$ and five $C_{20}H_{12}^+$ isomers colliding with He.

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 $C_N H_M$, there are many structural PAH isomers which may have very different chemical properties. As an example, the solubility in water of two $C_{14}H_{10}$ 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]+ complexes formed by electrospray ionization [19,20]. Some minor differences in the branching ratios between H- and C_2H_2-loss (the dominant dissociation channels for PAHs) have been observed following photo-absorption processes
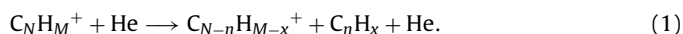
Table 1
Absolute fragmentation cross sections (10^{-15} cm^2) for PAH cation isomers in collisions with He atoms at 110 eV center-of-mass energy. Cross sections are given for losing at least one carbon atom ($C_{n\geq1}H_x$-loss) and exactly one carbon atom (CH_x-loss). In the bottom row we give the ground state energies (GSEs, eV) relative to the most stable isomer, as calculated by density functional theory (see text).

$C_N H_M{}^+$	$C_{16}H_{10}{}^+$			$C_{18}H_{12}{}^+$			
Isomer	**(1)** Pyrene	**(2)** Fluoranthene	**(3)** Benzo[b]biphenylene	**(4)** Chrysene	**(5)** Benz[a]anthracene	**(6)** Tetracene	**(7)** Triphenylene
$\sigma_{C_{n\geq1}H_x}$	2.0	1.9	2.1	2.2	2.1	2.0	1.8
σ_{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

$C_N H_M{}^+$	$C_{20}H_{12}{}^+$				
Isomer	**(8)** Benzo[e]pyrene	**(9)** Benzo[a]pyrene	**(10)** Perylene	**(11)** Benzo[b]fluoranthene	**(12)** Benzo[k]fluoranthene
$\sigma_{C_{n\geq1}H_x}$	1.9	2.2	2.1	2.1	2.2
σ_{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$^+$ cations and He atoms at center-of-mass energies around 100 eV:

$$C_N H_M{}^+ + He \longrightarrow C_{N-n}H_{M-x}{}^+ + C_n H_x + He. \qquad (1)$$

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.
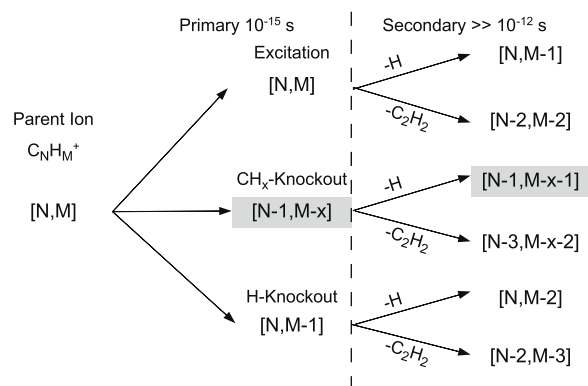

Fig. 1. Simplified diagram of the most important fragmentation channels for PAH cations $C_N H_M{}^+$. The numbers in brackets represent the number of C and H atoms remaining in the larger fragment on femtosecond time scales (left) and on time scales longer than picoseconds (right). Pathways resulting 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
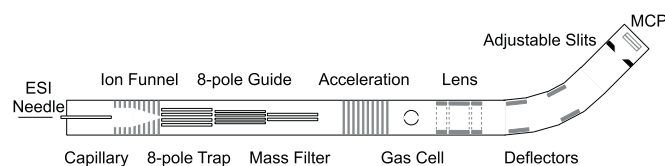

Fig. 2. Schematic of the electrospray ion source (ESI), collision cell and the electrostatic fragment analysis system with its position sensitive Microchannel Plate Detector (MCP).