Structural dynamics of PAH molecules upon energetic photon or ion interactions
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Chapter 2

Activation energies for fragmentation channels of anthracene dications - experiment and theory

We have studied the fragmentation of the polycyclic aromatic hydrocarbon anthracene (C\textsubscript{14}H\textsubscript{10}) after double electron transfer to a 5 keV proton. The excitation energies leading to the most relevant dissociation and fission channels of the resulting molecular dication were directly determined experimentally. Density functional theory calculations were performed to explore the potential energy surfaces on which the fragmentation dynamics proceed. There is clear experimental evidence for a dominance of fission into C\textsubscript{11}H\textsubscript{7}\textsuperscript{+}-C\textsubscript{3}H\textsubscript{3}\textsuperscript{+} over C\textsubscript{2}H\textsubscript{2}\textsuperscript{+} loss. The energetic ordering of the dissociation and fission channels and the kinetic energy releases are in good agreement with theoretical results. It can be concluded that the unique combination of experiment and theory presented here is an excellent tool to study fragmentation of complex molecular ions with unprecedented detail.

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2.1 Introduction

Infrared emission features of the interstellar medium (ISM) are generally attributed to fluorescence photon emission of UV-pumped Polycyclic Aromatic Hydrocarbons (PAHs). Therefore, PAHs are considered as an abundant and ubiquitous component of the ISM. PAHs dominate the temperature and charge balances of the ISM and are crucial for interstellar chemistry, e.g. serving as carriers for surface chemical reactions or supplying reactive hydrocarbon cations upon dissociative and non-dissociative ionization. For example, PAHs are exposed to stellar winds, energetic ions from supernova shock waves and the hot ionized gas behind these shocks [1, 2, 3]. Although a general consensus on the existence and important role of PAHs has been reached in the field of astrochemistry, it has to be noted that a few alternative scenarios attribute infrared emission features to other species (e.g. amorphous organic solids with aromatic-aliphatic character [4]). For the astrophysically relevant ion kinetic energies between several 10 eV and a few keV, ion interaction dynamics with larger molecular systems are particularly rich. Since processes such as electron capture [5], elastic interactions with molecular constituents [3] and inelastic interactions with the molecular valence electrons [3, 6, 7] all contribute strongly. In a first experimental study, in which keV H$^+$, He$^+$ and He$^{2+}$ ions interacted with anthracene, multiple ionization and extensive fragmentation was observed by means of high resolution mass spectrometry [6]. Similar observations were made for keV ion collisions with coronene, fluoranthene [8], pyrene [9], and PAH clusters [10]. These experiments gave a qualitative insight into the stability of small PAHs and possible fragmentation pathways.

Theoretical studies, which most often employ density functional theory (DFT) techniques, allow for the precise calculation of parameters such as dissociation energies and fission barriers of complex molecular systems. The complexity of the molecular potential energy surfaces usually requires that the relevant channels must be determined experimentally. In [11] the adiabatic dissociation energies and ionization energies for multiply charged PAHs were calculated. The choice of dissociation channels was guided by data on singly charged PAH cations produced by photons [12], low energy electrons [13] or collision induced dissociation [14]. In all cases H, H$_2$ and C$_2$H$_2$ loss were identified as the most important channels.

The last decades, a large amount of data on photo-ionization and dissociation of PAHs and related compounds has become available. For instance, synchrotron radiation was used to study stability limits of naphthalene [15] and the size dependent stability of a number of PAHs [12]. Fragment ion coincidences were studied after UV induced double ionization of naphthalene [16, 17] and azulene [17], which provided data on fragmentation kinetics of proto-type PAHs.

In this work, we present the first direct measurement of ion induced dissociation kinetics of multiply charged anthracene cations. The fragmentation channels are identified by coincident detection of fragment ions. The branching ratios for these channels are determined and correlated to the activation energies and fragment kinetic energies. These branching ratios deviate remarkably strong from the case of singly charged cations. Guided by this particularly comprehensive dataset on
excitation energy dependent PAH fragmentation, we performed DFT calculations to explore the potential energy surface (PES) of the molecule. The synergy of experiment and theory allows us to draw a picture of PAH fragmentation which is of unprecedented detail.

2.2 Experimental and computational approach

To directly investigate the energetics of fragmentation processes in PAH dications experimentally, we use the CIDE (Collision Induced Dissociation under Energy Control) method. In this method, the technique of double charge transfer [18, 19] is combined with coincidence mass spectrometry [20]. In an event-by-event mode, an ionization or fragmentation channel is correlated to the initial excitation energy of the molecule. In particular we investigate 5 keV proton collisions with anthracene, i.e. double electron capture processes of the type:

\[
\text{H}^+ + \text{C}_{14}\text{H}_{10} \longrightarrow \text{H}^- + \text{C}_{14}\text{H}_{10}^{2+*} \rightarrow \text{H}^- + \text{fragm}. \quad (2.1)
\]

For scattering angles close to zero, momentum transfer from the projectile to the molecule can be neglected. The nonexistence of stable excited states of H\(^-\) then implies that the kinetic energy loss \(\Delta E\) of the projectile is a measure of the energy deposited into the molecule. The following relation gives the excitation energy, \(E_{\text{exc}}\):

\[
E_{\text{exc}} = \Delta E - [I_{M1} + I_{M2} - I_H - EA_H], \quad (2.2)
\]

where \(I_{M1} = 7.44\) eV [21] and \(I_{M2} = 11.90\) eV [11] are the first two ionization energies of the anthracene molecule, and \(I_H = 13.6\) eV and \(EA_H = 0.75\) eV are the ionization energy and the electron affinity of hydrogen, respectively.

Details about the experimental setup can be found in previous publications [20, 22, 23]. Briefly, an effusive jet of anthracene molecules is produced by evaporating anthracene powder in an oven operated at 330 K. The jet is crossed with a collimated and focused proton beam (200 \(\mu\)m entrance slit), which is extracted at 5 kV from a 10 GHz ECRIS. In a coincidence event-by-event mode, the cationic collision products are analyzed by a time-of-flight (TOF) mass spectrometer and the projectile ion (H\(^-\)) energy is analyzed by an electrostatic analyzer (ESA). The ESA was calibrated by a reference experiment on Ar: \(\text{H}^+ + \text{Ar} \longrightarrow \text{H}^- + \text{Ar}^{2+}(1\text{D}_2)\).

The experimental results are interpreted with the help of DFT calculations carried out using the Gaussian09 package [24]. Molecular geometries were optimized and their frequencies were calculated at b3lyp/6-311G++(2d,p) level to determine the local minima (all real frequencies) and the transition states (one imaginary frequency). The quoted energies are zero point energy corrected (scaled with the factor 0.9877 [25]), and given relative to the ground state energy of the anthracene dication.
2.3 Results and discussion

Figure 2.1 shows a coincidence map of the TOFs of pairs of cationic reaction products formed after collisions with 5 keV protons. Islands due to $C_2H_x^+$, $C_3H_x^+$, $C_4H_x^+$, and $C_5H_x^+$, in coincidence with heavier anthracene fragments such as $C_{12}H_y^+$ are clearly visible. For each pair of fragments the excitation energy distribution was obtained from the projectile energy loss. From these distributions the most probable excitation energy was obtained by means of Gaussian fits. Figure 2.2 shows a zoom of the most prominent fission channel $C_{11}H_x^+$-$C_3H_y^+$ (central). The top and upper right panel show projections of the TOF of the light and heavy fragment, respectively. The associated excitation energy-TOF coincidence map is plotted in the lower left panel. The excitation energy distribution can be seen in the lower right panel. Table 2.1 lists all excitation energies and branching ratios of ten fragment-pair islands together with the respective excitation energy values for non-dissociative double ionization and for the $C_2H_2$ loss channel.
The excitation energies for the non-dissociative ionization channel and the C$_2$H$_2$ emission channel were determined from the singles TOF spectrum (figure 2.3). The C$_{12}$H$_8^+$ peak is the strongest one indicating that C$_2$H$_2$ loss is the dominant fragmentation channel for anthracene dications formed by double electron capture. Jochims et al. determined the internal energy of PAHs at fragment appearance and found the appearance energies associated with C$_2$H$_2$ and H$_2$ emission from VUV pumped anthracene monocations to be 8.42 eV and 9.75 eV, respectively. The trend of these values is to some extend comparable to the most probable ion induced excitation energies of emission from cations which we measured in the current work. For the fission processes C$_2$H$_x^+$ – C$_{12}$H$_y^+$, C$_3$H$_x^+$ – C$_{11}$H$_y^+$ and
Figure 2.3: A TOF-$\Delta E$ coincidence map (central) with a TOF projection (top) and a projection of the energy loss (right). The projections are plotted in red dotted and blue solid lines, which correspond to $\text{C}_{12}\text{H}_{8}^{2+}$ and $\text{C}_{14}\text{H}_{10}^{2+}$, respectively.

Table 2.1: An overview of the most relevant fragmentation channels; for every charged fragment pair the initial excitation energy and the branching ratios are listed. The doubly charged fragments are listed together with their associated excitation energies and their branching ratios.

<table>
<thead>
<tr>
<th>Channel</th>
<th>process</th>
<th>$E_{\text{exc}}$ (eV)</th>
<th>b.r</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}<em>{14}\text{H}</em>{10}^{2+}$</td>
<td>(non-dissoc.)</td>
<td>6.0</td>
<td>35.7</td>
</tr>
<tr>
<td>$\text{C}<em>{14}\text{H}</em>{8}^{2+}$</td>
<td>(2H$<em>{2}$/H$</em>{2}$ loss)</td>
<td>13 ± 1</td>
<td>-</td>
</tr>
<tr>
<td>$\text{C}<em>{12}\text{H}</em>{8}^{2+}$</td>
<td>(C$<em>{2}$H$</em>{2}$ loss)</td>
<td>10.2</td>
<td>25.0</td>
</tr>
<tr>
<td>$\text{C}<em>{12}\text{H}</em>{x}^{+} + \text{C}<em>{2}\text{H}</em>{y}^{+}$</td>
<td>(fission)</td>
<td>13.6</td>
<td>0.34</td>
</tr>
<tr>
<td>$\text{C}<em>{11}\text{H}</em>{x}^{+} + \text{C}<em>{3}\text{H}</em>{y}^{+}$</td>
<td>(fission)</td>
<td>12.9</td>
<td>1</td>
</tr>
<tr>
<td>$\text{C}<em>{10}\text{H}</em>{x}^{+} + \text{C}<em>{4}\text{H}</em>{y}^{+}$</td>
<td>(fission)</td>
<td>12.4</td>
<td>0.68</td>
</tr>
<tr>
<td>$\text{C}<em>{10}\text{H}</em>{x}^{+} + \text{C}<em>{2}\text{H}</em>{y}^{+}$</td>
<td>(loss+fission)</td>
<td>15.8</td>
<td>0.15</td>
</tr>
<tr>
<td>$\text{C}<em>{9}\text{H}</em>{x}^{+} + \text{C}<em>{3}\text{H}</em>{y}^{+}$</td>
<td>(loss+fission)</td>
<td>16.1</td>
<td>0.73</td>
</tr>
<tr>
<td>$\text{C}<em>{8}\text{H}</em>{x}^{+} + \text{C}<em>{4}\text{H}</em>{y}^{+}$</td>
<td>(loss+fission)</td>
<td>15.8</td>
<td>0.81</td>
</tr>
<tr>
<td>$\text{C}<em>{8}\text{H}</em>{x}^{+} + \text{C}<em>{2}\text{H}</em>{y}^{+}$</td>
<td>(loss+fission)</td>
<td>20.7</td>
<td>0.38</td>
</tr>
<tr>
<td>$\text{C}<em>{6}\text{H}</em>{x}^{+} + \text{C}<em>{2}\text{H}</em>{y}^{+}$</td>
<td>(loss+fission)</td>
<td>28.1</td>
<td>0.50</td>
</tr>
<tr>
<td>$\text{C}<em>{7}\text{H}</em>{x}^{+} + \text{C}<em>{3}\text{H}</em>{y}^{+}$</td>
<td>(loss+fission)</td>
<td>18.2</td>
<td>0.77</td>
</tr>
<tr>
<td>$\text{C}<em>{5}\text{H}</em>{x}^{+} + \text{C}<em>{3}\text{H}</em>{y}^{+}$</td>
<td>(loss+fission)</td>
<td>24.6</td>
<td>0.81</td>
</tr>
<tr>
<td>$\text{C}<em>{6}\text{H}</em>{x}^{+} + \text{C}<em>{4}\text{H}</em>{y}^{+}$</td>
<td>(loss+fission)</td>
<td>22.5</td>
<td>1.02</td>
</tr>
</tbody>
</table>
Figure 2.4 displays the shift of the position of the $C_{14}H_{10}^{2+}$ peak as a function of excitation energy. A clear shift from $m/q = 89$ ($C_{14}H_{10}^{2+}$) to $m/q = 88$ ($C_{14}H_{10}^{2+} - 2H/H_2$) is observed when the excitation energy increases from 4 to 14 eV. It is not possible to unambiguously resolve sequential emission of two hydrogen atoms and emission of molecular hydrogen which correspond to the same mass-to-charge ratio.

The double electron capture data can to some extent be compared to results from VUV photon induced naphthalene fragmentation investigated by means of photoelectron-photoion-photoion coincidence (PEPIPICO) spectroscopy [17]. For $C_4H_3^+ - C_{10}H_5^+$, we found most probable excitation energies of 13.6, 12.9, and 12.4 eV respectively. The excitation energies corresponding to two-body fission with an additional loss of $C_2H_2$ were all around 16 eV. Two-body fissions with multiple losses of $C_2H_2$ showed up at significantly higher excitation energies. $C_2H_2$ loss related processes are also prominent in the correlation diagrams (see fig. 2.1): For instance the yield of two-body fission events $C_3H_3^+ - C_{11}H_5^+$ is approximately half of the sum of the yields of the channels involving single or multiple $C_2H_2$ losses ($C_3H_3^+ - C_{11-2n}H_5^+ + nC_2H_2$). In general, $C_2H_2$ loss is associated with a relatively low excitation energy of 10.2 eV while for fission processes excitation energies of at least 12.4 eV are observed.

Additional important channels in the singles TOF spectrum are H and $H_2$ loss.
a photon energy of 40.8 eV, the double ionization energy of naphthalene, the maximum amount of energy deposited in the molecular dication is \( \approx 19 \) eV. If we adopt the qualitative composition of the coincidence islands from the naphthalene-D\(_8\) data and transfer this to anthracene, this would give us compositions for the upper three fission islands of anthracene: \( C_2H_2^+ + C_{12}H_{6,7,8}^+ + C_3H_2^+ + C_{11}H_{5,6,7}^+ + C_4H_2^+ + C_{10}H_{5,6,8}^+ \). Figure 2.2 shows a zoom of the \( C_3H_3^+ - C_{11}H_3^+ \) islands with these processes indicated by thin solid lines (central panel). The lower left panel shows that the excitation energy is rather constant for different possible processes in this coincidence island. In the coincidence spectra of reference [16] the branching ratios of the \( C_2H_2^+ + C_8H_7^+ + C_9H_7^+ + C_7H_7^+ \) and \( C_7H_7^+ + C_6H_7^+ \) channels are 1:0.6:0.6. In the naphthalene-D\(_8\) data at 13 eV and 19 eV deposited [17], this ratio is 1.0:0.4:0.6, respectively. In most of the cases the \( C_3H_3^+ - C_7H_7^+ \) processes dominate, but not as pronounced as in the present ion impact data.

To further investigate the delicate balance between the most prominent decay pathways for the anthracene dication, we have explored the potential energy surface for the lowest energy barriers associated with \( H, H_2 \), and \( C_2H_2 \) loss, as well as for the strongest fission channel (\( C_3H_3^+ \) loss). Figure 2.5 displays a schematic of these barrier heights as determined by the DFT calculations. The removal of a single \( H \) atom and the sequential loss of two \( H \) atoms require 5.0 eV and 9.7 eV (not shown), respectively. These are activated by C-H bond stretching, while the emission of a \( H_2 \) molecule is initiated by a \( H \) atom moving to a neighbouring C-H group [26, 27], from which \( H_2 \) may be formed via a transition state that corresponds to the highest barrier (5.0 eV) along this pathway. This indicates a preference for \( H_2 \) emission at the highest excitation energies considered here (fig. 2.4), rather than the sequential emission. However, one can not rule out the existence of possible pathways with different \( C_{14}H_9^+ \) isomers for which the sequential emission of \( H \) atoms would be favoured at higher excitation energies.

\( C_2H_2 \) loss from the anthracene dication is the competing channel found experimentally to dominate the dissociation dynamics. The potential energy surface for this channel may involve many different routes including outer ring openings and isomerization processes, which are typically initiated by hydrogen shifts prior to dissociation as e.g. demonstrated for singly charged anthracene [27] and for \( C_{10}H_8^+ \) isomers (azulene and naphthalene) [26]. Fig. 2.5 shows that 5.4 eV is required to emit \( C_2H_2 \) from an outer ring, while only 4.6 eV is required following isomerization to benz[a]azulene. The latter appears to involve similar transition states as isomerization from naphthalene to azulene, from which there are at least six different pathways [26]. The complexity of the potential energy surface prohibits to rule out the existence of even lower barriers for this channel, but as the barrier can never be lower than the dissociation energy for the separate \( C_{12}H_8^+ + C_2H_2 \) system (4.3 eV), the rate determining activation energy barrier is in the 4.3-4.6 eV range. Thus, the lowest-energy decay pathway corresponds to \( C_2H_2 \) loss, in excellent agreement with the experimental findings.

The most prominent fission channel, \( C_{14}H_{10}^+ \rightarrow C_{11}H_3^+ + C_3H_3^+ \), is associated with a most probable excitation energy of 12.9 eV (see table 2.1). Fig. 2.5 shows that emission of \( C_3H_3^+ \) occurs via an outer ring opening similarly to the \( C_3H_3 \)
loss mechanism of singly charged naphthalene [26]. In the present case a Mulliken charge distribution analysis of the transition state confirms that it is indeed energetically more favourable to emit C$_3$H$_3^+$ than C$_3$H$_3$, which readily explains the experimental observation. The calculated fission barrier for this channel is 6.3 eV, while the dissociation energy is 4.5 eV. The difference of these quantities is the Kinetic Energy Release (KER) for internally cold systems and amounts to 1.8 eV. Even if the number of H can not be precisely resolved, it is noticeable that the measured KER from 2.1 (1.8 eV) is in good agreement with the theoretical value.

Finally, we note that the ratios between the calculated energy barriers (E$_b$) and the measured internal excitation energies (E$_{exc}$) are very similar for the H$_2$ (5.0/13=0.38), C$_2$H$_2$ (4.6/10.2=0.45), and C$_3$H$_3^+$ (6.3/12.9=0.49) loss channels. This is consistent with the expected behaviour for significant decay on the $\mu$s timescale, where the rate according to an Arrhenius type decay is given by $k=Ae^{-E_b/E_{exc}}$. Calculation of the actual rates would require a full exploration of the potential energy surface taking into account all transitions states along all possible pathways. Such studies have been shown to be rather involved for smaller and less complex PAH systems [26], and are thus well beyond the scope of this work.
2.4 Conclusion

In conclusion, we presented a combined experimental and theoretical study on the energy dependent fragmentation of the PAH anthracene. This study gives an excellent insight in the connection between deposited internal energy, the potential energy surface of the particular molecules and the most prominent fragmentation channels and led to the following main conclusions: (i) The fragmentation of \( \text{C}_{14}\text{H}_{10}^+ \) is dominated by emission of \( \text{C}_2\text{H}_2 \), which is associated with a most probable excitation energy of 10.2 eV; The prominence of this channel is completely supported by the DFT calculations of a low energy pathway via isomerization to benz[a]azulene, associated with a 4.6 eV barrier. (ii) The experiments show that emission of H and \( 2\text{H}/\text{H}_2 \) are associated with excitation energies between 4 and 14 eV. The calculated pathway for \( \text{H}_2 \) emission is associated with a barrier of 5.0 eV, while sequential loss of atomic H requires 9.7 eV. This suggests that \( \text{H}_2 \) emission is favored over \( 2\text{H} \) emission at the considered excitation energies. (iii) The coincidence map showed that emission of \( \text{C}_3\text{H}_3^+ \) is dominating over emission of \( \text{C}_2\text{H}_3^+ \), with excitation energies of 12.9 and 13.6 eV, respectively. This is also consistent with the calculations, in which the \( \text{C}_3\text{H}_3^+ \) emission was found to be energetically more favourable than \( \text{C}_3\text{H}_3 \) emission, while the opposite relation was found for \( \text{C}_2\text{H}_3^+ \) versus \( \text{C}_2\text{H}_2 \) emission. This \( \text{C}_3\text{H}_3^+ \) channel does not show up in the fragmentation of singly charged anthracene.

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