Coincidence mass spectrometry study of double ionization of anthracene by 70 eV electron impact

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Abstract. Double ionization of anthracene molecules by 70 eV electron impact results in a number of prominent fragmentations producing two singly ionized fragments. In our experiment, ionized fragments were detected using a reflectron time-of-flight mass spectrometer. A field programmable gate array was used for the timing and the recording of mass spectra on an event-by-event basis. A detailed model of the coincidence data acquisition was developed, enabling us to reliably obtain the map of true coincidences. Our measurements show that fragmentations for which the total number of carbon atoms in the two singly ionized fragments is even are generally significantly stronger than fragmentations for which the total is odd. No fragmentations are observed for a total number of 13 carbon atoms. There are only very weak fragmentations where one of the fragments only contains one carbon atom. Most of the fragments have 2 or 3 hydrogen atoms. There are several fragmentations in which the larger fragment has 9, 10, 11 or 12 carbon atoms and 5, 6, 7 or 8 hydrogen atoms. Fragments with only carbon atoms and no hydrogen atoms are not present, and only few fragmentations are observed with a fragment containing only one hydrogen atom.

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) have been studied extensively in recent years, because of their relevance in astrophysical processes, in interstellar chemistry, and in the formation of molecules of astrobiological interest [1–3]. PAH molecules, clusters and nanograins are key to the chemical evolution of large carbonaceous molecules in space, and are considered to be molecular precursors for abiotic syntheses of materials required by the earliest forms of life. The study of these molecules is of high relevance for the understanding of the structure and dynamics of biomolecular systems on the nanometer scale.

PAHs strongly absorb vacuum ultraviolet photons emitted by hot stars and relax by infrared emissions that are observed for a variety of astrophysical sources. By comparison with laboratory spectra, the emission bands observed in the infrared spectra of these sources have been attributed to the presence of neutral and ionized PAHs. These sources include the diffuse interstellar medium, photodissociation regions, the edges of molecular clouds, reflection nebulae, young stellar objects, HII regions, star forming regions, planetary nebulae, novae, and comets [4].

The interaction of atoms and molecules in the gas phase and on dust grains with vacuum ultraviolet photons, ions and secondary electrons can lead to excitation, ionization and dissociation. Gas-phase reactions of multiply charged cations with atoms, molecules and electrons lead to charge reduction, charge separation and chemical bond formation, and these reactive processes govern the evolution of the PAH population in the interstellar medium [5, 6]. Several authors [7–9] have highlighted the importance of low energy electrons for astrochemical processes and planetary atmospheres.

A variety of laboratory studies of PAH molecules have shown clear evidence for the formation of multiply charged molecular ions in collisions with photons, ions and electrons. Several research groups have used coincidence techniques to investigate the decay of these multiply charged PAH ions.

Wehlitz [10] has reviewed the double photoionization of hydrocarbons and aromatic molecules using synchrotron radiation, and has discussed different mechanisms producing a doubly charged organic molecule. Several groups [11–14] have used coincidence techniques to investigate the double photoionization and the subsequent decay of a series of PAHs at fixed photon energy using several different light sources. Robson et al. [15] have studied the fragmentation of laser-desorbed anthracene, tetracene and pentacene in intense laser fields, showing the presence of doubly and triply charged fragments in the mass spectra. Hartman
et al. [16] have used a time-of-flight mass spectrometer to measure the ratios of doubly to singly charged molecular parent ions of several PAHs for photon energies ranging from 5 to 280 eV. Monfredini et al. [4] have studied the photoionization and photostability of naphthalene, anthracene, 2-methyl-anthracene, and pyrene using synchrotron light, and have determined absolute photoionization and photodissociation cross sections and the production rates of singly, doubly, and triply charged ions. Lee et al. [17] have investigated the dissociation and ionization dynamics of singly and doubly excited fluorene, phenanthrene and pyrene molecules in ultrafast time-resolved XUV-IR pump-probe experiments.

Several groups have investigated the formation of doubly charged PAHs in ion–molecule collisions (for a review see pages 8–9 in [18]). Several groups have measured mass spectra of different PAH molecules showing the clear presence of multiply charged fragments [19–21]. Martin et al. [22] have studied the fragmentation of doubly charged anthracene in collisions with F+ ions at 3 keV using the CIDEc method (collision-induced dissociation under energy control). Doubly or singly charged fragments resulting from the loss of neutrals (H, C2H2) or C2Hx+ (x = 1–5; y = 1–5) have been measured as a function of the excitation energy of the parent molecule C14H102+. Reitsma et al. [23] have applied coincidence mass spectrometry to the fragmentation of anthracene after double electron transfer to a 5 keV proton. Reitsma et al. [24] have measured charged collision products in coincidence in a recoil ion momentum spectrometer in 30 keV He2+ collisions with naphthalene molecules. Brédy et al. [25] have studied fragmentation of anthracene induced by collisions with 40 keV Ar8+ ions. Using a coincident detection technique, they measured mass spectra of anthracene ions differentiated by the charge r (1 ≤ r ≤ 4) of the parent ion C14H10r+.

In our earlier mass spectrometry studies of anthracene and phenanthrene [26, 27], we measured (non-coincident) mass spectra as a function of electron impact energy, and we found clear evidence for the production of doubly charged fragments. The mass spectra of singly charged ions produced by doubly and triply charged anthracene molecules have been obtained at 70 eV electron impact [28] and at 100 eV electron impact [29]. At 70 eV the preferred routes for charge separation of doubly charged anthracene ions lead to the singly charged fragments CH3+, C2H2+ and C2H3+. Multiply charged fragments have also been observed in PAH mass spectra of PAH molecules by other groups, for instance for coronene and corannulene [30].

The purpose of this paper is to report on the application of coincidence mass spectrometry to the study of double ionization of anthracene molecules by 70 eV electron impact. The technique we are using is event-by-event recording of ions using a single reflectron time-of-flight mass spectrometer.

2 Experiment

The experimental set-up consists of a molecular beam of anthracene, a pulsed electron beam, and a reflection time-of-flight mass spectrometer, contained in three inter-connected and differentially pumped vacuum chambers. The set-up has been used before for non-coincidence mass spectrometry of the nucleobases, anthracene [26] and phenanthrene [27].

The beam of anthracene molecules is generated by resistively heating a small oven containing anthracene powder (99% purity from Sigma-Aldrich) to a temperature of 100 °C. Molecules are effusing from a capillary (0.5 mm diameter and 4.5 mm length) in the oven and pass through a skimmer (1.2 mm diameter) into the collision chamber where they are collided with electrons. The electron gun is pulsed at a rate of 13.6 kHz with a 0.2 µs pulse width. The energy resolution of the electron beam is about 0.8 eV FWHM. Positively charged fragments are extracted into the mass spectrometer 0.04 µs after the electron pulse. The data set used in this paper was accumulated over 221 h and comprises 10.8 × 109 sweeps.

In our previous experiments [26, 27], the pulsing of the electron gun and the ion extraction voltage were controlled by a precision delay generator, and the data acquisition was done using a computer controlled multichannel scaler. In the present experiment, these pieces of equipment have been replaced by a National Instruments cRIO907 field-programmable gate array (FPGA) with a 9402 digital input/output module. We have developed extensive new LabVIEW code for the communication between the FPGA and a PC, running on the FPGA chassis, and for the control of the experiment and the data acquisition, running on the PC.

The FPGA is used to synchronously control the timings of the pulsing of the electron gun and the ion extraction voltage, and the recording of the arrival time of the ions at the detector on an event-by-event basis. For each electron pulse, the arrival times of the ions are recorded with a resolution of 12.5 ns. The arrival times are streamed to a data file on the PC in real time. If no ion is detected for a given electron pulse, only a zero representing a valid start is recorded in the data file. The resulting file holds the full record of all the sweeps, with zero, one or multiple ion detection events in each sweep.

3 Data analysis

C++ software has been developed to read the full data file, and to assemble a coincidence map for all electron pulses for which two or more ions were detected. It is important to carefully correct the raw coincidence data for random coincidences, and for the detector chain dead-time including the pulse forming electronics. To improve the accuracy of this correction, regardless of count rates, a full model of the detection process
was used to calculate the net, non-random, coincidence rates.

This model carefully considers the true and apparent rates of both non-coincident and coincident events, as well as the blocking effect of earlier detections due to the dead-time. The resulting nonlinear correction is applied successively to individual bins of both the non-coincident and coincident spectra. This is possible because the dead-time blocking factor for any particular bin, needed to determine the true rate, depends only on the true rates in the preceding bins and the true rate in the current bin. Because the true rates in the preceding bins are calculated in the preceding steps, the true rate in the current bin can be determined from the apparent rate. For a known dead-time function this approach is insensitive to the absolute magnitude of the overall and coincident event rates, as nonlinear saturation and blocking effects are fully accounted for. The only assumption that needs to be made is that the rates are stable. Because of this, the analysis of data is done in groups of data, obtained by summing over a section of 26 bins. The coincident-free diagonal band in Fig. 1 is the direct effect of the detector chain dead-time.

In our coincidence map all fragmentations producing two ions are appearing as bimodal distributions aligned approximately along the counter diagonal through the point \((t_1, t_2)\), where \(t_1\) and \(t_2\) are the nominal arrival times of both ions. In order to understand the shapes of these distributions, we have done trajectory simulations for two of the fragmentations:

\[
\begin{align*}
C_{14}H_{10}^{+} &\rightarrow C_3H_3^{+} + C_{11}H_7^{+} \quad (1) \\
C_{14}H_{10}^{+} &\rightarrow C_4H_2^{+} + C_6H_2^+ + \text{neutral fragments} \quad (2)
\end{align*}
\]

Figure 3 shows the measured and the simulated bimodal distributions for these fragmentations. Details on the trajectory simulations are given in the appendix.

When two ions are formed in a fragmentation following a double ionization, and their initial velocities are in opposite directions but directed along the flight path, the one ion will arrive slightly earlier at the detector and the other ion will arrive slightly later, compared to the nominal arrival times. The result is that the extension of the bimodal distributions along the counter diagonal is a measure of the energy available in the dissociation producing the two singly charged ions. The energy distributions for the two simulations extend from 0 to 3.8 eV with a peak at around 2.0 eV. The energy is divided between the two fragment ions assuming a total momentum of zero. Many of the ions formed with initial velocities perpendicular to the main flight path are not detected, because they hit the MCP detector outside the active surface area, and this results in a depletion in the central area of the bimodal distributions.

The bimodal distributions also have a width along the diagonal through the point \((t_1, t_2)\), where \(t_1\) and \(t_2\) are the nominal arrival times of both ions. This width is due to the finite size of the interaction region along the extraction field direction, formed by the overlap of the molecular beam and the electron beam. In the simulations the spatial extend of the interaction region was taken to be 0.7 mm FWHM so that the simulated distributions match the width of the observed distributions.

4 Results and discussion

As in our previous paper [26], we identify groups of peaks in our mass spectra by the number of carbon atoms contained in the fragments. Group 14 is the parent ion group, containing the masses 174 u to 180 u. Group 7 contains integer masses, and this group contains singly charged fragments with 7 carbon atoms and doubly charged fragments with 14 carbon atoms. In the non-coincident mass spectrum, the ions in group 14 have the highest abundance, followed by the ions in groups 7 and 6.

Double ionization processes can be written as

\[
e^- + C_{14}H_{10} \rightarrow C_{14}H_{10}^{+} + 3e^- \rightarrow C_{8}H_{m}^{+} + C_{6}H_{n}^{+} + 3e^- + \text{neutral fragments}
\]

As noted in the previous section, in our coincidence map all fragmentations producing two ions are appearing as bimodal distributions aligned approximately along the counter diagonal through the point \((m_1, m_2)\), in which \(m_1 = (12a + m)\) u and \(m_2 = (12b + n)\) u. In the following discussions, we indicate the coincidence groups as \((a, b)\) where \(a\) and \(b\) are the number of carbon atoms in each of the fragments.

4.1 The full coincidence map

Figure 1 shows the full coincidence map. The mass scales are plotted such that the scales are linear in flight time. The color scale is in counts and the colors have been chosen in such a way that both strong fragmentations (in yellow–red-pink colors) and weak fragmentations (in shades of blue) are clearly visible. Negative counts (in green) arise from the correction for random coincidences and are due to the statistical uncertainties in the rates of true and random coincidences, and these are statistically consistent with non-negative values.

Before we discuss the most relevant coincidence groups in more detail, a number of overall observations can be made from Fig. 1. Fragmentations for which the total number of carbon atoms in both fragments is even are generally significantly stronger than fragmentations for which the total is odd. Strong fragmentations are
observed for groups \((a, b)\) with \(a + b = 8, 10, 12\) and 14, and weaker fragmentations are observed for \(a + b = 7, 9\) and 11. Interestingly, no fragmentations are observed for groups with \(a + b = 13\).

Reitsma et al. [23] have made the same observation in a coincidence map of singly charged fragments from anthracene dications produced by 5 keV \(H^+\) impact on anthracene. Similarly, the coincidence map of singly charged fragments produced by 30 keV \(He^{2+}\) ions on naphthalene \((C_{10}H_8^+)\) show very weak fragmentations of groups \((a, b)\) with \(a + b = 9\) [24]. Lee et al. [17] have observed that the fragmentation of doubly charged fluorene, phenanthrene, and pyrene molecules produced by XUV laser pulses also favors reaction pathways involving two-body breakup with loss of neutral fragments totaling an even number of carbon atoms.

Lawicki et al. [20] have observed even–odd oscillations with the number of carbon atoms, \(n\), in the intensity distributions of the \(C_nH_x^+\) fragments produced in collisions of multiply charged ions with pyrene and coronene. They state that these oscillations indicate a linear chain structure of the fragments and are due to dissociation energy differences between even- and odd-\(n\) \(C_n\)-chain molecules. However, this is not directly comparable to our data in Fig. 1, because for example, we do not see any clear differences in the yields in the groups \((4, 6)\) and \((4, 8)\) compared to \((3, 7)\) and \((3, 9)\).

In Fig. 1, the strongest fragmentations are in the groups \((a, b) = (3, 5), (3, 7), (3, 11)\) and \((4, 6)\). In these four groups the strongest fragmentations are \(C_3H_5^+ + C_5H_5^+, C_3H_5^+ + C_7H_5^+, C_3H_5^+ + C_{11}H_5^+\) and \(C_4H_7^+ + C_6H_7^+.\) The diagonal groups \((4, 4)\) and \((5, 5)\) show weaker fragmentations.

Fig. 1 The full coincidence map for ions produced by double ionization of anthracene by electron impact. Both scales are linear in ion flight time, and the mass scales are adjusted accordingly. The color scale shows the content of individual bins.
Fig. 2 Coincidence mass spectrum for 63 u (C_5H_3^+). This spectrum has been extracted from the full coincidence map by summing over 26 bins covering a range from 62.5 to 63.5 u. Above 120 u no coincidences are expected and this spectrum shows the reliability of our correction for random coincidences.

Fig. 3 Top row: the fragmentation C_3H_3^+ + C_11H_3^+: a probability distribution for the total fragmentation energy modeled as the sum of two beta distributions, b modelled coincidence map using a Monte-Carlo trajectory simulation, c a small section of the measured coincidence map. Bottom row: the fragmentation C_4H_2^+ + C_6H_2^+: d probability distribution for the total fragmentation energy, e modelled coincidence map using a Monte-Carlo trajectory simulation (the neutral fragments were not included in the simulation), f a small section of the measured coincidence map. See the Appendix for details on the simulations. The color scales are the same as in Fig. 1.
anthracene ions lead to the singly charged fragments produced routes for charge separation of doubly charged PAH molecules. We note that we do not observe where one of the fragments has only carbon atoms.

There are only very weak fragmentations producing fragments of equal mass. There are no clear fragmentations in group (7, 7).

Kingston et al. [28] noted that at 70 eV the preferred routes for charge separation of doubly charged anthracene ions lead to the singly charged fragments CH$_3^+$, C$_2$H$_2^+$ and C$_3$H$_3^+$. In our coincidence map fragmentations producing C$_3$H$_3^+$ are prominent, but fragmentations producing C$_2$H$_2^+$ have higher yields than those producing C$_3$H$_3^+$. CH$_3^+$ are very weak. Chacko et al. [31] highlight the importance of small hydrocarbon cations in the interstellar medium, and note hydrocarbon cations with H/C ratios higher than one such as CH$_4$-$^+$ and C$_2$H$_3$-$^+$ cannot form via direct photodissociation of PAH molecules. We note that we do not observe cations like this in the fragmentation of doubly charged anthracene.

In two locations, weak fragmentations are observed with one fragment of half-integer m/q. We interpret these as fragmentations following triple ionization, and the observed fragmentations are CH$_3^+$ + C$_{13}$H$_7^{++}$ and C$_3$H$_3^+$ + C$_{11}$H$_7^{++}$.

4.2 Fragmentations with one larger and one smaller fragment

Figure 4 shows the nine most relevant coincidence groups (a, b) with a ≤ b ≤ 7. In all these groups, fragmentations in which each of the fragments has 2 or 3 hydrogen atoms are the most prominent. Fragmentations in which one of the fragments has only 1 hydrogen atom are generally very weak, and are absent in groups (2, 6) and (4, 6).

Group (4, 10) shows that formation of C$_4$H$_4^+$ + C$_{10}$H$_8^+$ occurs much more prominently than formation of C$_4$H$_4^+$ + C$_{10}$H$_6^+$, showing that after two C–C bond breakages, the transfer of two hydrogen atoms is likely. In our non-coincident mass spectra [26] we observed that C$_{10}$H$_8^+$ has an appearance energy of 18.4 eV, whereas C$_{10}$H$_6^+$, has an appearance energy of 23.2 eV.

The coincidence groups (6, 8) and (5, 9) require two C–C bond breakages in the middle ring of the doubly charged parent, and the much lower coincidence yields in these two groups shows that these fragmentation processes are much less likely. The strongest fragmentation in both these groups is C$_5$H$_3^+$ + C$_5$H$_5^+$.

The coincidence groups (4, 8), (3, 9), (2, 8) and (2, 10) all show Coulomb fragmentations that are accompanied by one or more neutral fragments containing a total of 2 or 4 carbon atoms and a few hydrogen atoms. The most prominent fragmentation is C$_2$H$_3^+$ + C$_3$H$_3^+$ possibly including a neutral C$_2$H$_4$ fragment. Also prominent in these groups are C$_2$H$_2^+$ + C$_6$H$_2^+$, C$_4$H$_2^+$ + C$_6$H$_6^+$ and C$_3$H$_2^+$ + C$_8$H$_2^+$.

Very noticeable is that several fragmentations are clearly not occurring. Examples are C$_3$H$_2^+$ + C$_6$H$_4^+$ in group (3, 9), C$_3$H$_2^+$ + C$_{11}$H$_4^+$ in group (3, 11), C$_2$H$_2^+$ + C$_{10}$H$_4^+$ in group (2, 10), and C$_2$H$_2^+$ + C$_{12}$H$_{15}$ in group (2, 12). It is difficult to understand this in terms of a simple empirical model. In our previous measurements [26] clear evidence was observed for the rearrangement of hydrogen atoms in the fragmentation of anthracene, and this may be why certain combinations of two charged fragments are unlikely to be formed.

4.3 Fragmentations with two smaller fragments

Figure 5 shows the six most relevant coincidence groups (a, b) with a ≤ b ≤ 7. In all these groups, fragmentations in which each of the fragments has 2 or 3 hydrogen atoms are the most prominent. Fragmentations in which one of the fragments has only 1 hydrogen atom are generally very weak, and are absent in groups (2, 6) and (4, 6).

Following from the Monte-Carlo trajectory simulations (see discussion above), in all of the fragmentations observed, the amount of energy available in the Coulomb fragmentation peaks at about 2.0 eV. The exception is in group (2, 6), where the fragmentation C$_2$H$_2^+$ + C$_6$H$_4^+$ shows a larger extend along the counter diagonal, indicating that about 3.0 eV is available in this fragmentation. The reason for this is not clear to us.

In group (3, 5) the bimodal distributions clearly have slightly different angles, which indicates that some of the fragments involved may lose an additional hydrogen atom while they are travelling in the first field-free region of the reflectron time-of-flight mass spectrometer.
Fig. 4 Sections of the measured coincidence map for nine coincident groups \((a, b)\) with \(a \leq 6\) and \(b > 7\), where \(a\) and \(b\) are the number of carbon atoms in the two fragments. Each section contains 160 \(\times\) 160 bins and corresponds to \(2 \times 2\) µs in ion flight time. The mass scales are adjusted accordingly. The color scales are the same as in Fig. 1.

4.4 The formation of stable doubly charged fragment ions

In our earlier study of anthracene [26] we measured a series of mass spectra for positive ions in which the electron impact energy was varied from 0 to 100 eV in steps of 0.5 eV. These mass spectra clearly showed significant ion yields for non-integer masses in groups 1 to 7. The smaller fragments with 1 to 4 carbon atoms all clearly showed broadened peaks, and we interpreted these fragments as due to Coulomb fragmentations of doubly charged anthracene. The ion yields observed for non-integer masses in group 5 were interpreted to be partly due to doubly charged fragments at half-integer masses and partly due to broadened peaks of singly charged fragments at integer masses. No half-integer masses were observed in groups 8 to 14.

This raises the question to what extent the Coulomb fragmentations observed in our coincidence measurements contribute to the yields of non-integer fragments observed in our non-coincident mass spectra in [26]. Our present coincidence data clearly shows that the bimodal
Fig. 5 Sections of the measured coincidence map for six coincident groups \((a, b)\) with \(a \leq b \leq 7\), where \(a\) and \(b\) are the number of carbon atoms in the two fragments. Each section contains \(160 \times 160\) bins and corresponds to \(2 \times 2\) \(\mu\text{s}\) in ion flight time. The mass scales are adjusted accordingly. The color scales are the same as in Fig. 1.

distributions produced by the Coulomb fragmentations are expected to produce signals at non-integer masses in the non-coincident mass spectra.

We have compared the full non-coincident mass spectrum obtained from the present data set with the mass spectrum obtained by summing over all rows in the coincidence map. The latter mass spectrum has yields that are about a factor 50 (for group 2) to 500 (for groups 12 and 14) lower than the yields in the full non-coincident mass spectrum. We conclude that the contributions from the Coulomb fragmentations to the non-coincident ion yields in groups 8 to 14 are very small. It is difficult to directly compare these two mass spectra. Because of its high kinetic energy, an ion of a particular mass produced in a Coulomb fragmentation is much less likely to be detected than an ion of the same mass produced in a fragmentation after single ionization.

In group 7, we observed [26] that the ratio of 89.5 u to 89 u is equal to the isotope ratio 179 u / 178 u, and that this ratio is constant from 100 eV down to about 30 eV (below this energy the data lacks statistics). We concluded that 89 u is almost entirely \(\text{C}_{14}\text{H}_{10}^{++}\). This was also observed by Robson et al. [15] in femtosecond laser mass spectrometry and by Postma et al. [19] in ion impact mass spectrometry. Based on these observations we attributed the half-integer peaks in group 7 to doubly charged fragments. In groups (3, 7) and (5, 7) in Fig. 5 almost no coincident fragmentations are observed for 88 u and 89 u. There is larger scatter at these masses because these masses have high yields in the non-coincident mass spectrum. This supports the conclusion in our previous paper [26] that 89 u is almost entirely \(\text{C}_{14}\text{H}_{10}^{++}\).

We also observed [26] that the 77.5 u / 77 u ratio was slightly lower than the isotope ratio and approximately constant between 30 and 100 eV. A similar observation of the 76.5 u / 76 u ratio was made by Wacks and Dibeler [32]. In groups (2, 6) and (4, 6) in Fig. 5 few coincident fragmentations are observed for 76 u and 77 u, which suggests that a large part of the 76 u and 77 u yields are due to doubly charged ions.

The coincident groups in Fig. 5 show prominent fragmentations in which each of the fragments has 2 or 3 hydrogen atoms. These Coulomb fragmentations contribute to the yields of half-integer masses observed in groups 5, 6 and 7 in the non-coincident mass spectrum, but it is not clear by how much, and it is likely that doubly charged fragments contribute to the yields in these groups as well.
Böhme [6] has reviewed the importance of multiply charged ions for the chemistry in the interstellar medium. In this context, our study of the fragmentation processes of doubly charged anthracene is of relevance. Several groups have measured mass spectra in ion–molecule collisions of different PAH molecules, showing that it is possible to produce multiply charged fragments in electron transfer collisions [19–21]. Banhatti et al. [33] have measured infrared spectra of the PAH dications naphthalene$^{2+}$, anthracene$^{2+}$, and phenanthrene$^{2+}$, which were produced by 70 eV electron impact ionization of the vapours.

5 Conclusion

We have used coincidence mass spectrometry to the study of double ionization of anthracene molecules by electron impact. Our measurements show that fragmentations for which the total number $a + b$ of carbon atoms in both fragments (see Eq. 3) is even are generally significantly stronger than fragmentations for which the total is odd. Strong fragmentations are observed for groups $(a, b)$ with $a + b = 8, 10, 12$ and 14, and weaker fragmentations are observed for $a + b = 7, 9$ and 11. No fragmentations are observed for $a + b = 13$. There are only very weak fragmentations where one of the fragments only contains one carbon atom. The strongest fragmentations are in the groups $(a, b) = (4, 6), (3, 5)$ and $(3, 7)$, in particular $C_8H_2^+ + C_6H_2^+$, $C_5H_3^+ + C_5H_3^+$, and $C_3H_3^+ + C_7H_3^+$. The diagonal groups $(4, 4)$ and $(5, 5)$ also contain a few strong fragmentations, but because of detector chain dead-time fragmentations producing fragments of exactly equal mass are not fully resolved.

Most of the fragments have 2 or 3 hydrogen atoms. In the groups $(a, b)$ with $a \leq 6$ and $b > 7$ there are several fragmentations in which the larger fragment has 5, 6, 7 or 8 hydrogen atoms. The strongest fragmentations are in the groups $(a, b) = (4, 10), (3, 11)$ and $(2, 12)$, in particular $C_7H_2^+ + C_10H_6^+, C_5H_3^+ + C_11H_7^+, and C_2H_4^+ + C_12H_6^+$. Fragments with only carbon atoms and no hydrogen atoms are not present. In a few places we observe fragments with only one hydrogen atom, for instance in group $(3, 5)$ weak fragmentations are $C_3H_23^+ + C_5H^+$, and $C_3H^+ + C_5H_23^+$. 

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Author contribution

The application of the field programmable gate array for the recording of mass spectra on an event-by-event basis and the associated programming was done by MG. The model of the coincidence data acquisition used for the extraction of the map of true coincidences was developed and implemented by MG. The measurements and the trajectory simulations were done by PvdB. PvdB wrote most of the paper, and MG contributed to the discussion of the results.

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Data availability This manuscript has associated data in a data repository. [Authors’ comment: The full data set associated with this manuscript will not be uploaded to an online repository, but this data set is available from the corresponding author on reasonable request.]

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Appendix

This appendix provides the details on the trajectory simulations and the simulated bimodal distributions that are show in the top right and bottom right of Fig. 3. These simulations have been implemented in Python. The trajectory of each singly charged ion is calculated using a particle-in-cell simulation [34, 35], covering the interaction region, the first and second acceleration stages, and Einzel lens of the reflectron time-of-flight mass spectrometer. The position and the components of the velocity vector of the ion at the exit of the Einzel lens are then used to calculate the arrival time and the position of the ion when it hits the detector. In this latter calculation the deceleration and acceleration of the ion in the reflector are accounted for.

For the particle-in-cell part of the simulation, the electric potential is obtained by numerically solving the Laplace equation in a 2-dimensional configuration with cylindrical symmetry. This configuration contains 240 × 60 cells with a cell size of 0.396875 mm = 1/64", and fixed potentials are set at the positions of the two extraction plates with mesh-covered holes, and the three cylindrical elements of the Einzel lens. The ion
trajectory calculations are done in 3 dimensions, in which the electric field vector at the position of the ion is calculated by interpolation using the 2-dimensional electric potential combined with cylindrical symmetry.

The bimodal distributions are obtained by doing trajectory calculations for a total of 500,000 ion pairs and using their calculated arrival times to build up the simulated bimodal distribution. Each ion pair is generated at a random point in the interaction region, with the ions ejected in opposite directions (180° apart) with a random ejection angle, and a random total energy determining the initial speeds of the ions. The random point in the interaction region is generated using 3 Gaussian probability distributions with equal FWHMs of 0.70 mm. The random ejection angle is generated by taking a random point on a sphere.

The random total energy \( E \) in the Coulomb fragmentation is obtained by using a probability distribution \( f(E) \) which is the sum of two beta distributions:

\[
f(E) = E_0 \left\{ pf \left( \frac{E}{E_0}; \alpha_1, \beta_1 \right) + (1-p) f \left( \frac{E}{E_0}; \alpha_2, \beta_2 \right) \right\}
\]

By varying the parameters \( \alpha_1, \beta_1, \alpha_2, \beta_2, E_0 \) and \( p \), a wide variety of distributions can be generated. In order to generate the simulated bimodal distributions, a number of trial simulations were done until a good agreement with the observed distributions was obtained, as shown in Fig. 2. For the 39 u + 139 u fragmentation we used

\[
f(E) = E_0 \left\{ 0.34 \times f \left( \frac{E}{E_0}; 1.7, 2.1 \right) + 0.66 \times f \left( \frac{E}{E_0}; 6.0, 4.0 \right) \right\},
\]

and for the 50 u + 74 u we used

\[
f(E) = E_0 \left\{ 0.42 \times f \left( \frac{E}{E_0}; 1.7, 2.1 \right) + 0.58 \times f \left( \frac{E}{E_0}; 4.5, 4.0 \right) \right\},
\]

with \( E_0 = 3.8 \text{ eV} \) in both cases. These distributions are shown in Fig. 2a, d.

Apart from an Einzel lens after the initial acceleration our reflectron mass spectrometer (R. M. Jordan) does not contain any focusing elements. The Einzel lens was optimized in the past for the detection of thermal ions, and provides a small correction for the finite size of the interaction region from which the ions are extracted. For Coulomb fragmentations the Einzel lens provides negligible focussing, but in doing the simulations we found that a small amount of focusing is introduced at the extraction plate that the ions pass through, because the mesh covering the hole in the plate is spot-welded on one side. In our simulations in Fig. 2 both ions are detected for only about 12% of the ion pairs generated.

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