Abstract. We have measured the ratio of doubly to singly charged parent ions of pyrene, an aromatic hydrocarbon, for photon energies ranging from threshold to the carbon K edge. Monochromatized synchrotron radiation of the Synchrotron Radiation Center has been used in combination with an ion time-of-flight spectrometer for this investigation. We compared these results with our previous measurements on benzene, coronene and pyrrole. We will discuss differences and similarities in the double photoionization for these aromatic hydrocarbons.

1. Introduction
In 1967 Carlson [1] reported the observation of a “double electron ejection” from the outermost shell of an atom using an X-ray tube. This experiment started a series of experiments on double photoionization using synchrotron radiation, in which two electrons are excited into the continuum by a single photon. This so-called double photoionization process has been studied extensively for atoms and smaller molecules using different experimental techniques. Naturally, helium became the textbook example for this process and many investigations using various experimental setups from ion yield measurements to electron coincidence measurements (see, e.g., [2] and references therein).

After reaching a satisfactory agreement between theory and experiment for the double-to-single photoionization ratio of helium over a wide energy range, investigations on heavier elements commenced. Ion-yield measurements on lithium, beryllium, sodium, potassium and magnesium demonstrated that the photon-energy dependence of that ratio is very similar to the one for helium if the energy axis is given in units of the energy difference between the corresponding double- and single-ionization thresholds [3]. It was also found that double K-shell photoionization exhibits the same energy dependence for the ratio as valence double photoionization.

However, it was not known if the properly scaled energy dependence of the ratio will be the same for molecules as for atoms. Our measurements on C$_{60}$ demonstrated that the double-to-single photoionization ratio is affected by the structure of the molecule [4] and does indeed show a much different energy dependence. If the initially emitted photoelectron has a kinetic energy that corresponds to a de Broglie wavelength that matches a geometrical distance in the C$_{60}$ molecule, so that a standing wave can be formed, then the electron stays longer in the molecule and increases thereby the probability for double ionization. As a result, the double-to-single photoionization ratio of C$_{60}$ shows enhancements at certain energies that correspond...
to de Broglie wavelengths equal to the diameter of the molecule, or the diameter of a hexagon formed by the carbon atoms, or the distance between two adjacent carbon atoms. Moreover, small enhancements in the ratio have been seen also at energies corresponding to fractions of these distances.

From the C\textsubscript{60} experiment we concluded that the structure of a molecule can affect the double-to-single photoionization ratio. In order to further investigate this effect, we extended our research to aromatic hydrocarbons, which are rather stable and have a simple structure.

Recent investigations on acenes, chains of one to five benzene rings, demonstrated the existence of at least three different double-photoionization mechanisms [5]. One of the mechanisms, that is already known from atomic double photoionization, is the "knock-out" of another electron by the photoionized electron. This notion of an internal collision has been suggested by Samson [6] based on the similarity of the excitation energy dependence between the double-to-single photoionization ratio of an atom and the electron-impact cross section of the corresponding singly charged ion. At any fixed energy less than 30 eV above threshold, where the knock-out mechanism is dominant, the ratio of doubly to singly charged acene parent ions rises linearly with the length of the molecule [7].

The second double-photoionization mechanism, that we found in acenes, is the brief formation of a pseudoparticle consisting of two electrons, which can be regarded as a Cooper pair. This pair breaks up into two individual electrons after it is photoemitted from the molecule [8]. This mechanism, however, does not exist for aromatic molecules with a pentagonal structure such as pyrrole, furan, thiophene and selenophene.

The third mechanism that we have observed for aromatic molecules leads to a linear increase of the ratio above a certain photon energy. Above even higher energies this ratio starts to increase even faster than linearly. The perfect linear increase of the ratio indicates that a particular mechanism is at work, but the origin of this effect is still unknown.

In this paper we report of our results for pyrene (C\textsubscript{16}H\textsubscript{10}), which is an aromatic molecule consisting of four benzene rings arranged in a diamond shape. In contrast to our previous investigations, this molecule is not a linear chain of benzene rings, and is smaller than the previously studied coronene (C\textsubscript{24}H\textsubscript{12}).

2. Experiment

Two experiments were performed at the Synchrotron Radiation Center (SRC) in Stoughton, WI (USA). One experiment was conducted on the 6-meter toroidal-grating monochromator (6m-TGM) beamline [9] using photon energies from 18 to 170 eV. The second experiment was conducted on the varied line-spacing plane-grating monochromator (VLS-PMG) beamline [10] using energies from 150 to 280 eV. The monochromatic photon beam entered through a differential pumping stage into the interaction region inside the vacuum chamber, where the photon beam crossed an effusive beam of thiophene molecules vaporized in a resistively heated oven. The oven temperature was kept at around 34 °C.

A pulsed electric field accelerated the photoions and photofragments towards a drift tube with a Z stack of microchannel plates at its end. The pulse period was 0.1 ms so that only long-lived metastable or fully stable ions were detected. More details regarding the experiment and data analysis can be found in [5].

We have detected doubly and singly charged molecular parent ions of pyrene (C\textsubscript{16}H\textsubscript{10}). While fragments are clearly visible in our ion spectra, we do not consider them here. Stability of a molecule is of practical importance to keep the probability for fragmentation low. In particular, the breakup of a molecule into two fragments of the same mass has to be avoided when measuring the mass-to-charge ratio of a molecular ion or fragment. Otherwise the doubly charged parent ion appears at the same position in the ion time-of-flight spectrum as the singly charged fragment with half the mass of the molecule. Fortunately, the pyrene molecule did not noticeably break
3. Results and discussion

Figure 1 shows an ion time-of-flight spectrum with the doubly and singly charged parent ions and fragments. As can be seen, the peaks of the doubly as well as singly charged parent ions are affected by fragments, which appear as shoulders of the parent-ion peaks. We have tried to extracted the areas of both parent-ion peaks by employing a least-squares fit. However, this fit did not yield reliable results as the peak separation was difficult. Instead, we determined the fraction of the parent-ion area to the total area of that peak region as a function of photon energy. The resulting “fraction” curve was then smoothed since we do not expect any sudden changes in the fragmentation but anticipate a smooth change of this fraction. This procedure was performed for both parent-ion peaks. The ratio of the areas of both peak regions was then corrected for with both fraction curves, so that we obtained the ratio of doubly charged to all (singly plus doubly charged) parent ions as a function of photon energy.

The ratio of the doubly charged to all (singly plus doubly charged) parent ions in the threshold region is shown in figure 2. We applied a least-squares fit to the near-threshold data using a power function:

\[ R_a(h\nu) = a(h\nu - E^{2+})^n + b. \]  

(1)

Here, \( h\nu \) is the photon energy, \( E^{2+} \) the threshold energy, \( a \) a fit parameter, \( n \) an exponent and \( b \) an additional offset. This empirical method to determine the double-ionization threshold has been used in the past and was referred to as the “nth power rule” \[11\] meaning an approximately parabolic fit for double ionization. A small offset \( b \) was included in the fit function to take care of any remaining doubly charged ion signal due to second-order light or scattered light. The threshold energy obtained for pyrene is \((19.28 \pm 0.03)\) eV.

In figure 3 we show the ratio of doubly charged to all parent ions of pyrene from threshold to the carbon K edge. As in the case of other hydrocarbons \[5\] such as, e.g., pyrrole and furan, we see a straight linear increase of the ratio above about 80 eV. We have tried to fit a helium ratio curve to the pyrene ratio at lower energies but the fit program did not find a stable solution.
Figure 2. Ratio of doubly charged to all parent ions of pyrene as a function of photon energy (full circles). The full line is a fit curve to the data (see text for details).

Figure 3. Ratio of doubly charged to all parent ions of pyrene (blue dots with error bars connected by a full line) as a function of photon energy. The straight broken line emphasizes the linear increase of the ratio above a certain energy. The dotted line is the scaled double-to-total photoionization ratio of helium [12] (see text for details). The arrows point at two humps in the ratio curve.
Figure 4. Ratio of doubly charged to all parent ions of pyrene (full circles with error bars) in the low photon-energy region. The dotted line is the scaled double-to-total photoionization ratio of helium [12] (see text for details). The full line is a fit to the low energy data.

In a previous investigation on acenes we have found that the ratio scales with the length of the molecule [7]. Pyrene, however, is not a chain of benzene rings but a system of four benzene rings in two dimensions. We already know that in the case of coronene, which is a ring of six benzene rings, the scaling for the ratio is 6.2 [5]. Thus, we assume that the ratio scales approximately with the area of the molecule. We have plotted in figure 3 a helium ratio curve scaled for four benzene rings, i.e., dividing the helium ratio by 0.93 (which reproduces the benzene ratio at low energies) and then multiplying it by 4.0 to account for the four benzene rings. With an additional energy scaling of these data we achieve a reasonably well fitting curve to the pyrene data shown as a dotted line in figure 3. As a result, we have now characterized two of the three double photoionization mechanisms, namely the knock-out mechanism (area beneath the dotted line) and the mechanism that leads to a linear increase of the ratio (area between the broken line and the dotted line).

Furthermore, one can see two humps in the pyrene ratio data marked with arrows in figure 3. As we will see later, the hump at the higher energy corresponds to the formation of a Cooper pair that has a de Broglie wavelength of the carbon–carbon distance in the molecule. This hump has already been seen for the acenes [8]. In addition one can see another hump at lower energies. In order to make this hump better visible we show the low-energy region of the pyrene ratio in figure 4 in more detail. Again, the dotted line represents the double photoionization via the knock-out mechanism. The full line is the threshold fit as discussed above. At about 24 eV both lines overlap and the threshold curve merges into the knock-out curve. At about 30 eV one can see a clear enhancement of the pyrene ratio.

Figure 5 displays the ratio of doubly to singly charged parent ions of pyrene after subtracting the contribution of the knock-out mechanism (dotted line in figure 3). Two prominent humps are visible before the ratio increases at higher energies. This linear increase of the ratio with increasing excess energy is steeper than for benzene and pyrrole. The broad hump around 50 eV with its onset near 40 eV, corresponding to a de Broglie wavelength of 1.4 Å, has been seen before for the acenes [8], e.g., benzene. It is worthwhile to note that the magnitude and width
Figure 5. Ratio of doubly to singly charged parent ions of pyrene (full black circles), benzene (open red squares), pyrrole (open blue circles) and coronene (full green triangles) after subtracting the contribution from the knock-out mechanism (see text for details). The upper abscissa displays the de Broglie wavelength of a two-electron pseudoparticle.

of this hump is very similar to the one for the acenes.

The narrower hump near 10 eV corresponds to a de Broglie wavelength of 2.8 Å or twice the carbon–carbon distance in the molecule. This hump has been seen so far only for coronene [8]. Both molecules, coronene as well as pyrene, consist of benzene rings fused in two dimensions, i.e., are not linear chains of benzene rings such as the acenes. This allows for the formation of a closed-loop de Broglie wave with twice the carbon–carbon distance because the curvature of that loop is large enough. The “end-ring” in the acenes, however, requires the de Broglie wave to take a rather sharp turn, which prevents it from forming a closed-loop with a long wavelength of 2.8 Å. In the extrem case of benzene the closed loop with a wavelength of 2.8 Å forms a triangular shape. Pyrene and coronene, on the other hand, are large enough to support a long wavelength. Interestingly, the hump near 10 eV is as tall as the hump near 50 eV for pyrene whereas the low-energetic hump of coronene is smaller than the high-energetic hump.

4. Summary
We have measured the ratio of doubly to singly charged parent ions of pyrene, an aromatic hydrocarbon consisting of four fused benzene rings arranged in a diamond shape. This ratio is approximately four times higher than the one for benzene as expected for a molecule that has an area four times the one for benzene. This finding confirms our model that the ratio increases not only with the length of the molecule, as for the acenes, but also with the area of the molecule, namely pyrene with a ca. 4 times and coronene with a 6.2 times larger ratio than benzene due to the knock-out mechanism. This scaling supports the notion that one of the double-ionization mechanisms is indeed the knock-out mechanism.

Qualitatively the pyrene ratio behaves similarly to the ratio for the acenes with a broad hump.
around 50 eV excess energy and a straight linear increase of that ratio above 70 eV. However, in contrast to the acenes the pyrene ratio exhibits a second hump near 10 eV excess energy corresponding to the formation of a closed-loop de Broglie wave with a wavelength of twice the carbon–carbon distance.

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