

**Isomer effects in the double-to-single photoionization ratio of aromatic hydrocarbons**T. Hartman,<sup>1</sup> K. Collins,<sup>2</sup> and R. Wehlitz<sup>1,\*</sup><sup>1</sup>*Synchrotron Radiation Center, University of Wisconsin–Madison, Stoughton, Wisconsin 53589, USA*<sup>2</sup>*College of Education, Purdue University, West Lafayette, Indiana 47907, USA*

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We have measured the ratios of doubly to singly charged molecular parent ions of azulene and phenanthrene, which are isomers of naphthalene and anthracene, respectively. The photon-energy dependences of the ratio curves have been analyzed and compared to each other from threshold to the carbon *K* edge. Qualitatively, the ratio curves for azulene and naphthalene as well as phenanthrene and anthracene are very similar, but we have found a distinct quantitative difference in both cases for the two isomers.

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**I. INTRODUCTION**

The double-photoionization process, in which two electrons are simultaneously removed from an atom or molecule, is due to electron correlations [1]. The ongoing study of double-photoionization mechanisms in aromatic molecules provides important information on electron correlation in these molecules, as well as providing a basis for further understanding of radiation damage in large biomolecules [2]. It has been described previously how the relative size of a molecule affects the double-to-total photoionization ratio among different aromatic molecules. The ratio as a function of excess energy (photon energy minus the double-ionization threshold) was shown to be linearly proportional to the length of the molecule (or approximately proportional to the number of rings in the linear row) for the linear acenes benzene, naphthalene, anthracene, and pentacene [3]. While this ratio has been precisely shown to be a linear function of length, additional questions arise, such as whether more subtle changes in the length of the molecule will cause a similar effect in the ratio curve. In other words, can different isomers cause a change in the double-photoionization process?

Isomer effects have been studied previously in terms of their effects on electron-impact ionization [4], their scattering of low-energy electrons [5], their elastic scattering of low-energy electrons [6,7], and the effects of photofragmentation [8]. Isomers (molecules with the same molecular formulas but different arrangements of the atoms or the bonds connecting them) are divided into two main classes. The class of *constitutional* isomers includes molecules that have a different structure; i.e., the geometrical arrangement of atoms is different. In the second class of isomers are *stereoisomers*, which have the same bond structure within the molecule, but the positioning of atoms and functional groups is different [9].

The impact of structural changes upon the double-to-single photoionization ratio in structural isomers has been identified in this project to very good precision for two specific cases and offers further proof for the aforementioned model, in which the length of a linear acene plays an important role.

**II. EXPERIMENT**

Two different beamlines at the Synchrotron Radiation Center (SRC) in Stoughton, WI (USA), have been used in this investigation. The experiments were performed on the 6-m toroidal-grating monochromator (6m-TGM) beamline [10] with a bending-magnet source for photon energies from 17 to 170 eV and on the varied-line-spacing plane-grating monochromator (VLS-PGM) beamline with an undulator source [11] for energies from 150 to 280 eV. Details of similar experiments have been given elsewhere [2]. In brief, the monochromatic photon beam entered through a differential pumping stage into the interaction region inside the vacuum chamber where the beam crossed the target molecules. 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 Ref. [2].

We have detected doubly and singly charged molecular parent ions of azulene (C<sub>10</sub>H<sub>8</sub>) and phenanthrene (C<sub>14</sub>H<sub>10</sub>). The results for naphthalene and anthracene have already been published in Ref. [2] and are shown here for comparison only. The molecules' structures are displayed in Fig. 1 for reference. Data analysis has been performed as described in Ref. [2]. We note that the calculated ratio of doubly to singly charged parent ions pertains only to stable or long-lived metastable parent ions. While fragments are clearly visible in our ion spectra, they were not considered in this investigation. Instead, we focused on the parent ions that cannot be created by dissociation processes. It is also worthwhile to mention that the azulene high-energy spectra were taken between collecting two sets of naphthalene spectra, which minimizes systematic errors.

**III. RESULTS AND DISCUSSION****A. Azulene and naphthalene**

Figure 2 shows azulene and naphthalene spectra for comparison. While both spectra look quite similar overall, there are a few differences in the fragmentation pattern. However, in this paper we concentrate on the singly and doubly charged parent ions only.

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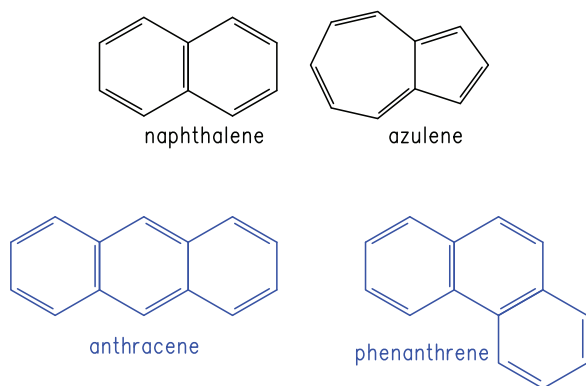


FIG. 1. (Color online) Azulene and phenanthrene, studied in this investigation, and their isomers naphthalene and anthracene.

Although the objective of our measurements was not to determine the double-ionization threshold of azulene (and thus the rather small number of data near threshold), we did determine the threshold as shown in Fig. 3. We applied a least-squares fit to the near-threshold ratios using a power function:

$$R_s(h\nu) = a(h\nu - E^{2+})^n + b. \quad (1)$$

Here,  $h\nu$  is the photon energy,  $E^{2+}$  is the threshold energy,  $a$  is a fit parameter,  $n$  is an exponent, and  $b$  is an additional offset. This empirical method to determine the double-ionization threshold has been used in the past [12,13] and was referred to as the “ $n$ th power rule” [12], 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 obtained for azulene is  $(20.93 \pm 0.12)$  eV, which is slightly lower than the one for naphthalene [(21.39  $\pm$  0.11) eV [2]].

Figure 4 shows the ratio of doubly to singly charged parent ions of azulene and naphthalene over an extended range of

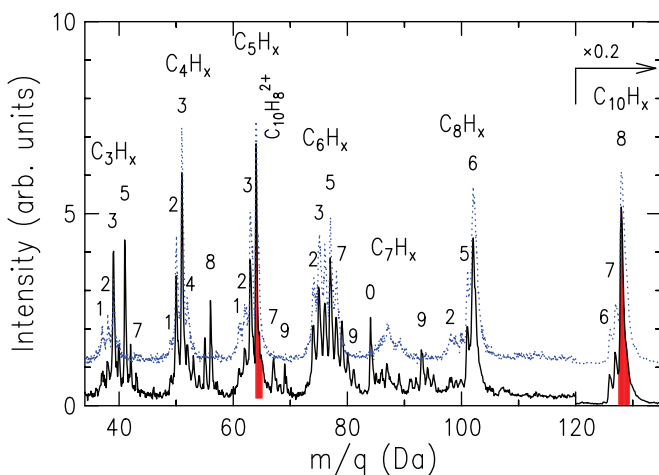


FIG. 2. (Color online) Mass-to-charge spectra of azulene (black solid line) at 130 eV and naphthalene (dotted line, blue online) at 149 eV photon energy. The singly and doubly charged parent ions are shaded in gray (red online). Note that the naphthalene spectrum is offset for better visibility.

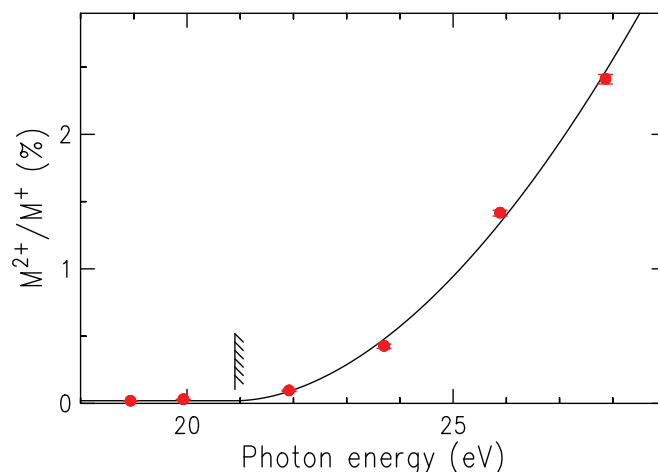


FIG. 3. (Color online) Ratio of doubly to singly charged parent ions of azulene near the double-ionization threshold along with a fit curve. The threshold as determined from the fit is indicated.

photon energies. Both ratio curves exhibit very similar photon-energy dependence but the azulene ratio is always slightly higher than the one for naphthalene—a clear indication that the ratio of doubly to singly charged parent ions depends on the structure of the molecule and not just on its constituents.

Like the naphthalene molecule, the azulene molecule has three distinct features in the ratio curve. At low energies, the curve can be scaled to match the helium ratio curve [14] (shown as a gray dotted line in Fig. 4). At medium energies, the ratio sees a hump that is caused by the formation of Cooper pairs when the excess energy allows for the formation of a de Broglie wave with a wavelength matching the carbon-carbon distance in the molecule. Since it has been shown that the Cooper pair formation occurs only in molecules with an even number of atoms in the ring [15], we believe that the de Broglie wave in azulene is not formed in the individual rings (which have five and seven atoms, both odd numbers of atoms), but around the perimeter of the ring as a whole, which has 10 atoms.

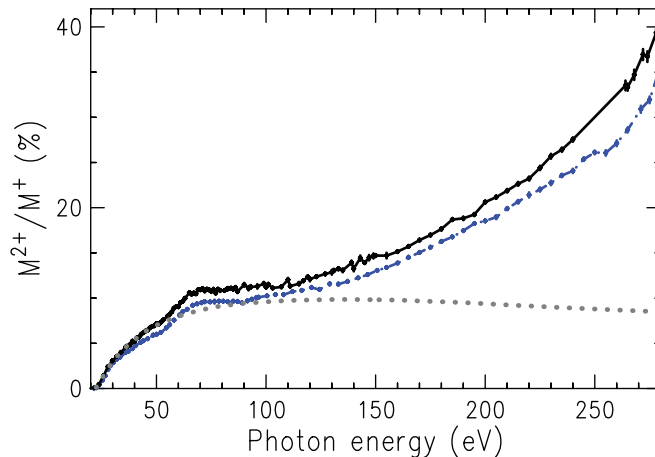


FIG. 4. (Color online) Ratio of doubly to singly charged parent ions of azulene (black dots connected by a solid line) and naphthalene (blue dots connected by a dashed line) as a function of photon energy. The dotted, gray curve is a He ratio curve [14] scaled in height to match the azulene ratio curve at energies below 52 eV.

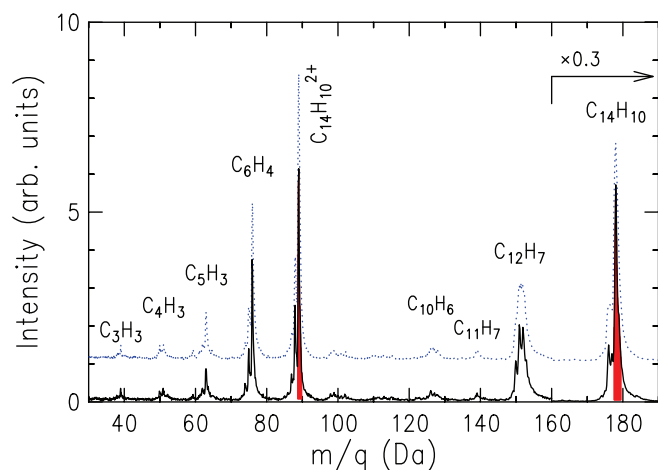


FIG. 5. (Color online) Mass-to-charge spectra of phenanthrene (black solid line) and anthracene (dotted line, blue online) both taken at 70 eV photon energy. The singly and doubly charged parent ions are shaded in gray (red online). Note that the anthracene spectrum is offset for better visibility.

Thus, azulene demonstrates the formation of a closed-loop de Broglie wave around the entire molecule, rather than just around the individual rings. At high energies, the ratio for the azulene molecule increases at a similar rate to naphthalene.

Overall, the azulene ratio lies slightly above the naphthalene ratio, and looking at the relative sizes of the molecules gives a plausible reason for this difference. The lengths of the two molecules are similar, but the area of the azulene molecule is slightly larger than that of naphthalene. While the pentagon of azulene is smaller than the two hexagons of naphthalene, the heptagon is much larger, and its larger size more than compensates for the smaller size of the pentagon. This slightly larger size allows for a slightly larger chance for the photoionized electron to interact with a second electron, causing it to also be emitted as explained by the knock-out model [16,17]. Hence, the azulene ratio is slightly higher than the one for naphthalene.

### B. Phenanthrene and anthracene

Figure 5 shows phenanthrene and anthracene spectra for comparison. Overall, both spectra look very similar, and there is no obvious difference in the fragmentation pattern. The peaks of singly and doubly charged parent ions of phenanthrene are shown as shaded areas.

As for azulene we determined the double-ionization threshold of phenanthrene using Eq. (1). The resulting fit curve is shown in Fig. 6. The double-ionization threshold obtained for phenanthrene is  $(20.17 \pm 0.25)$  eV, which is practically the same as for anthracene [ $(20.07 \pm 0.17)$  eV [2]] considering the error bars.

Figure 7 shows the ratio of doubly to singly charged parent ions of phenanthrene and anthracene over an extended range of photon energies. The ratio curves show similar photon-energy dependences but the phenanthrene ratio is always slightly lower than the one for anthracene. Again, this is a clear indication that the ratio of doubly to singly charged parent ions depends on the particular structure of the molecule.

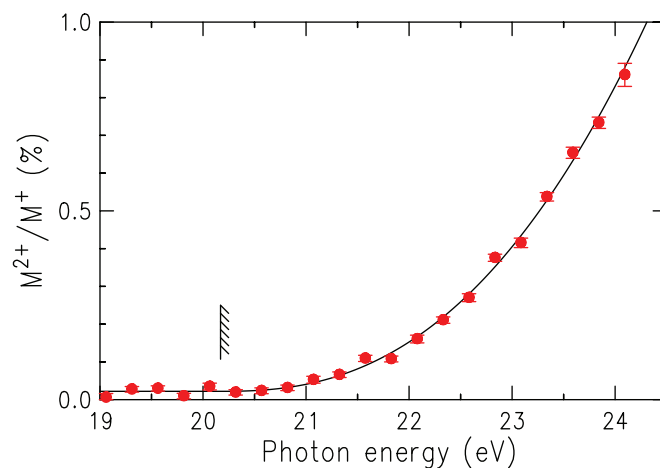


FIG. 6. (Color online) Ratio of doubly to singly charged parent ions of phenanthrene near the double-ionization threshold along with a fit curve. The threshold as determined from the fit is indicated.

Also in this case, the ratio curve of the phenanthrene molecule has three distinct features. At low energies, the curve can be scaled to match the helium ratio curve (shown as a gray solid line in Fig. 7). At medium energies, we obtain a hump due to the formation of Cooper pairs with their de Broglie wavelengths matching the carbon-carbon distance in the molecule. At high photon energies, the ratio for the phenanthrene molecule increases at a similar rate to anthracene.

The small difference in the two ratio curves is mainly attributed to a difference in the contribution from the knock-out mechanism at all energies. Since the contribution from the knock-out mechanism to the double ionization process depends on the length (or area) of the molecule, the slightly shorter phenanthrene molecule relative to anthracene has a lower ratio. So, the somewhat compressed structure of the phenanthrene molecule causes the ratio of doubly to singly charged parent ions to be slightly decreased, which provides

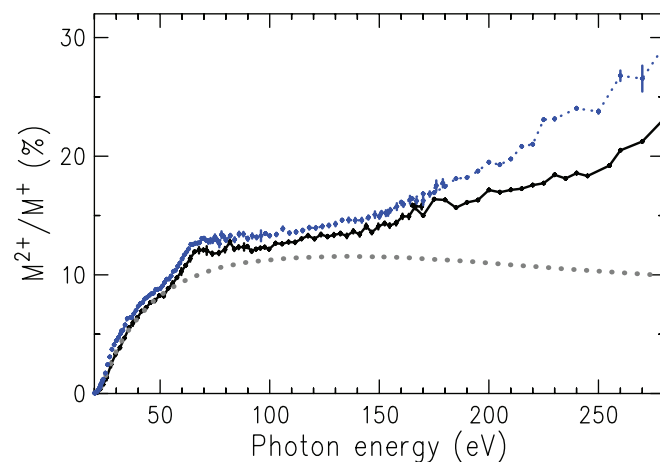


FIG. 7. (Color online) Ratio of doubly to singly charged parent ions of phenanthrene (black dots connected by a solid line) and anthracene (blue dots connected by a dashed line) as a function of photon energy. The dotted gray curve is a scaled He ratio curve [14] to match the phenanthrene ratio curve at energies below 53 eV.

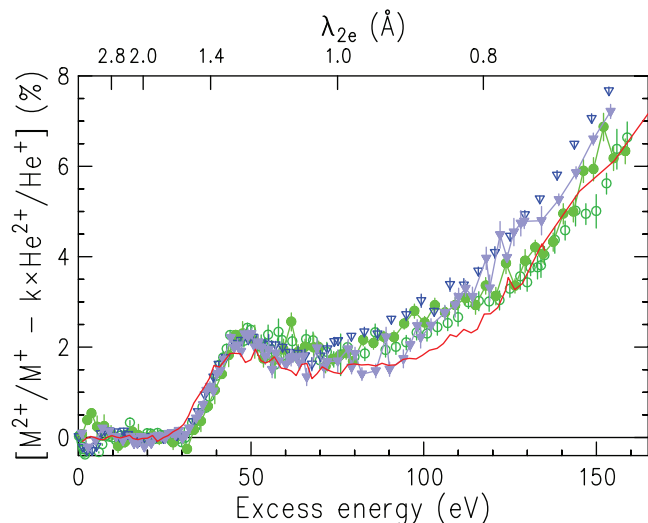


FIG. 8. (Color online) Ratio of doubly to singly charged parent ions after subtracting the contribution from the knock-out mechanism for benzene (solid line, red online) [2], azulene (filled triangles), naphthalene (open triangles), phenanthrene (filled circles), and anthracene (open circles). The upper abscissa shows the de Broglie wavelength of a Cooper pair.

further evidence for the length scaling model introduced in Ref. [3].

#### IV. SUMMARY

In summary, we have investigated double photoionization of phenanthrene and azulene, which are constitutional isomers of anthracene and naphthalene, respectively. For both the anthracene-phenanthrene pair as well as the naphthalene-azulene pair, we obtain a clear difference in the ratio of doubly to singly charged parent ions for the two isomers. Qualitatively, we find three distinct mechanisms that contribute to the creation of doubly charged parent ions as we found previously for other aromatic hydrocarbons [2]. The contribution of the knock-out mechanism (as represented by the gray dotted lines

in Figs. 4 and 7) is slightly more prevalent in the larger isomers azulene and anthracene. For the naphthalene-azulene case, the scaling factor for the He ratio curve (cf. Fig. 4) is 17% larger for azulene than for naphthalene. For the anthracene-phenanthrene case, the scaling factor for the He ratio curve (cf. Fig. 7) is 5% smaller for phenanthrene than for anthracene. This provides further evidence for the scaling model described earlier [3].

After subtracting the scaled He ratio curves, which represent the contribution from the knock-out mechanism, from the molecules' ratios, we see in Fig. 8 that the remaining ratio values are very similar for each molecular pair. This means that apparently only the knock-out mechanism is sensitive to the specific structure of an aromatic molecule. Other mechanisms contributing to the double-photoionization process as visualized in Fig. 8 are not (or only very little) affected by the structure of the molecule, which also means that although the fragmentation of molecules may be different for different isomers (see, e.g., Fig. 2), the creation of doubly and singly charged parent ions is not significantly affected by the fragmentation in the cases discussed here.

We also see an increased ratio starting at about 30 eV excess energy. This hump has the same position, width, and magnitude for azulene and phenanthrene as well as the previously discussed aromatic hydrocarbons in Ref. [15]. The increase in the ratios towards higher energies is slightly stronger for both azulene and naphthalene, whereas this increase is slightly smaller for phenanthrene and anthracene.

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