

## Large Molecules Reveal a Linear Length Scaling for Double Photoionization

T. Hartman,<sup>1</sup> P.N. Juranić,<sup>1,\*</sup> K. Collins,<sup>2</sup> B. Reilly,<sup>3</sup> N. Appathurai,<sup>1</sup> and R. Wehlitz<sup>1,†</sup>

<sup>1</sup>*Synchrotron Radiation Center, University of Wisconsin-Madison, Stoughton, Wisconsin 53589, USA*

<sup>2</sup>*University of Evansville, Evansville, Indiana 47714, USA*

<sup>3</sup>*University of Wisconsin-Madison, Madison, Wisconsin 53706, USA*

(Received 27 July 2011; published 10 January 2012)

We have measured the ratio of doubly to singly charged parent ions of benzene, naphthalene, anthracene, and pentacene using monochromatized synchrotron radiation up to 30 eV above the corresponding threshold. Our measurements show a striking similarity between the ratio of doubly charged to all parent ions and the ratio for helium. Moreover, the magnitudes of the ratios for these molecules scale linearly with their lengths with an amazing accuracy. A high ratio, i.e., a high relative double-photoionization probability, makes a molecule an important source of low-energy electrons that can promote radiation damage of biomolecules [B. Boudaïffa *et al.*, *Science* **287**, 1658 (2000)].

DOI: 10.1103/PhysRevLett.108.023001

PACS numbers: 33.80.Eh

Double photoionization, i.e., the simultaneous emission of two electrons due to absorption of a single photon, is a fundamental process that helps to elucidate electron correlations in atoms and molecules. Numerous investigations of the double-photoionization process have been performed on atoms [1–3] and small molecules [4–8] in the past, though larger molecules consisting of more than five atoms have been somewhat neglected in this respect. Doubly charged benzene ions have been investigated in only very limited energy ranges [9,10], and naphthalene dications have been investigated at two photon energies [11]. Two of the general open questions are how the structure of a molecule affects the double-photoionization process, and where the two emitted electrons originate. It is important to stress that simultaneous double photoionization produces electrons with kinetic energies ranging from 0 eV to an upper limit (photon energy minus double-ionization threshold) with, generally, many electrons near 0 eV [12]. Low kinetic energy electrons are known to cause radiation damage to biomolecules [13,14] through attachment. Therefore it is important to know double-ionization rates for larger molecules.

In this Letter, we present experimental results for the photoionization ratio of doubly to singly charged parent ions of structurally similar molecules (acenes) with different lengths consisting of 12 to 36 atoms. Our results presented here always refer to the stable or long-lived metastable parent ions; i.e., we investigated the ratio of doubly to singly charged ions that have the same mass as the molecule under investigation. In the following, this is just called the ratio  $R_s$ . Likewise, the ratio of doubly charged to *all* (singly plus doubly charged) parent ions is denoted as  $R_a$ . The lengths of the molecules investigated here vary with respect to the structure of their carbon atoms from 2.8 Å for benzene [15] to 14 Å for pentacene [16], which consists of five fused benzene rings and is also the longest stable chain of fused benzene rings. We discovered

that the ratio  $R_a$  of doubly charged parent ions to all parent ions increases perfectly linearly with the lengths of the molecules for photon energies up to at least 30 eV above the double-ionization threshold. The dramatic increase of the ratio  $R_a$  by a factor of 5 for pentacene as compared to the ratio of benzene can be understood in terms of the knockout model that was previously introduced for atoms by comparing the double-to-single photoionization ratio to the electron-impact single-ionization cross section of a singly charged ion [17]. Our results provide direct evidence of this model for the first time without the need for using electron-impact data for comparison.

Experiments on partially deuterated benzene ( $C_6H_3D_3$ ) [18], naphthalene ( $C_{10}H_8$ ) [19], anthracene ( $C_{14}H_{10}$ ) [20], and pentacene ( $C_{22}H_{14}$ ) [21] were performed at the Synchrotron Radiation Center using monochromatized synchrotron light on the 6 m toroidal grating monochromator beam line [22]. The liquid benzene was freeze-pump-thawed 3 times to remove gases from the vial holding the sample. The vial holding the powder naphthalene was pumped for about 30 minutes before use. Anthracene (powder) had to be warmed up in a crucible to 33 °C to achieve a sufficient vapor pressure. Pentacene was vaporized using a resistively heated oven at a temperature of about 185 °C. The chamber's base pressure was in the mid  $10^{-9}$  mbar range. The sample gas pressure was about  $1.0 \times 10^{-6}$  mbar.

An ion time-of-flight spectrometer, operating in the pulsed-extraction mode, separated the ions of different mass-to-charge ratios [23]. The pulse period was 0.1 ms so that only long-lived metastable or fully stable ions were detected. We have used *partially deuterated* benzene because the fragment  $C_3H_3^+$  and the doubly charged parent ion  $C_6H_6^{2+}$  have the same mass-to-charge ratio whereas  $C_6H_3D_3^{2+}$  does not have a corresponding fragment of the same mass-to-charge ratio.

The measured ratios  $R_s$  for partially deuterated benzene, naphthalene, anthracene, and pentacene are shown in Fig. 1. The excess energy scale, defined by the incident photon energy minus the corresponding double-ionization threshold, allows us to conveniently compare the photon-energy dependence of the ratios for all four molecules.

As mentioned above this ratio pertains only to stable or long-lived metastable parent ions. It is well known that molecules can also dissociate into singly and doubly charged fragments after photoionization. Those fragments are clearly visible in our spectra but were not considered in this investigation. Instead, we focused on the parent ions that cannot be created by dissociation processes. One can disentangle the dissociative pathways for small molecules using photoelectron-photoion-photoion coincidences (see, e.g., [4–6,11]) but this is difficult to do for large molecules. Thus, the ratio of the true double-to-single photoionization cross sections will be different due to fragmentation processes. An overview of the photoionization dynamics in molecules can be found in [25]. The numbers of doubly and singly charged *parent* ions are most likely to be larger right after photoionization than at the time when the ions are detected (about 100  $\mu$ s later) after fragmentation has occurred. In this respect, our measured ratio is a simplified double-to-single photoionization ratio for molecules, which can be determined reliably in a straight forward manner. Because of the very similar bonds of the molecules presented here, we expect that dissociation processes are similar too.

From Fig. 1 it is evident that the ratio  $R_s$  for each molecule is smoothly increasing with increasing excess energy. In addition, each ratio curve is higher with increasing length of the molecule. Note that a few ratio values of anthracene and pentacene show some excursion from a

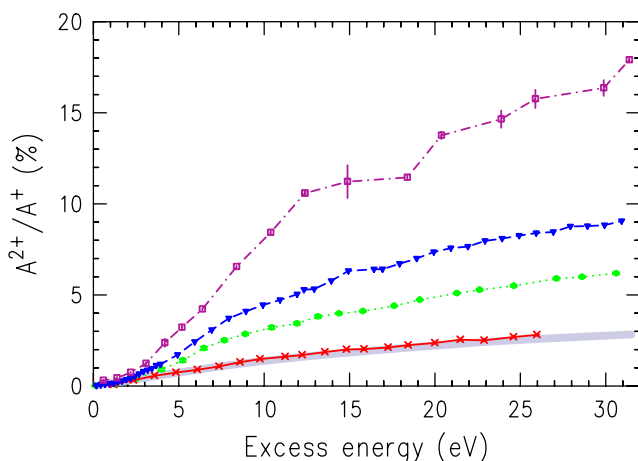


FIG. 1 (color online). The ratio  $R_s$  of stable parent ions of partially deuterated benzene (crosses), naphthalene (circles), anthracene (triangles), and pentacene (squares) as a function of excess energy. For comparison, the He double-to-single photoionization ratio is shown as a grey curve [24].

perfect curve possibly due to instabilities of the photon beam or from vaporizing the samples.

In order to determine the double-ionization thresholds of the four molecules, we applied a least-squares fit to the near-threshold ratios using a power function:  $R_s(h\nu) = a(h\nu - E_{\text{thr}})^n$ . Here,  $R_s$  is the measured ratio,  $h\nu$  the photon energy,  $E_{\text{thr}}$  the threshold energy,  $a$  a fit parameter, and  $n$  an exponent. This empirical method to determine the double-ionization thresholds has been used in the past [9,26] and was referred to as the “ $n$ th power rule” [9] meaning a parabolic fit for double ionization. We have used  $n$  as fit parameters that were between 1.7 and 2.3.

The double-ionization thresholds are presented in Table I showing that they decrease with increasing size of the molecule. There is qualitative agreement between different experiments, but the values differ from each other more than one would expect based on the error bars pointing to a more general experimental problem.

To investigate the increase of the ratio with increasing length of the molecules, we first calculated the ratio of doubly charged to all parent ions  $R_a$  from  $R_s$  using

$$R_a = 1 / \left( \frac{1}{R_s} + 1 \right). \quad (1)$$

This calculation neglects any triple and higher multiphoton ionization, which one can assume to be very small. Then we normalized the ratios  $R_a$  of each molecule to match the benzene ratio curve. The normalization factors for naphthalene, anthracene, and pentacene are 2.01(4), 2.88(8), and 5.02(5), respectively, (Fig. 2). Interestingly, these numbers not only correspond closely to the number of benzene rings the molecules consist of, but also represent the relative length of each molecule very well within their  $1\sigma$  (or  $2\sigma$ , for naphthalene) error bars.

This scaling clearly demonstrates that the ratio  $R_a$  increases linearly with the lengths of the molecules with an impressive accuracy for energies up to at least  $\approx 30$  eV above the double-ionization threshold. For the first time a proportionality of the ratio with the length of a molecule has been observed for a distance of up to 14 Å.

Figure 3 visualizes the proportionality by plotting the normalization factor  $N$  as a function of the length of the molecule. As mentioned above, we have used the molecular structure given by the carbon atoms to measure the

TABLE I. Double-photoionization thresholds for benzene (1), naphthalene (2), anthracene (3), and pentacene (5) given in eV. Note that we have used partially deuterated benzene ( $C_6H_5D$ ) whereas Refs. [27,28] have used  $C_6H_5D$ .

mol.	this work	[27]	[28]	[9]	[10]
1	24.92(7)	25.3(2)	26.4(5)	26.1(2)	24.6(1)
2	21.39(11)	21.5(2)	22.7(5)		
3	20.07(17)	19.6(2)	21.1(5)		
5	18.62(21)	17.4(2)			

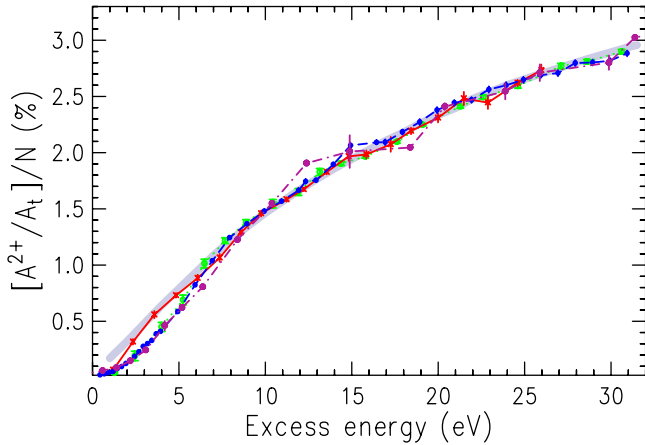


FIG. 2 (color online). Doubly charged parent ions relative to all parent ions normalized by  $N$ : partially deuterated benzene ( $N = 1.0$ , crosses), naphthalene ( $N = 2.01$ , circles), anthracene ( $N = 2.88$ , triangles), and pentacene ( $N = 5.02$ , squares). The He double-to-total photoionization ratio (gray curve) [24] is normalized by  $N = 0.93$ .

length of the molecules. The dashed straight line connects all four values extremely well.

This result indicates that the longer the molecule is, the more likely it is that the photon-absorbing electron can knock out a second electron on its way out. This behavior can be explained by extending the “two-step-one” [29] mechanism, which is also called the “half-collision” model [30] or “knockout” model [31], from atoms to molecules. The knockout model has been previously identified for atoms [17,32]. It has been found that the double-to-total photoionization ratio is proportional to the electron-impact single-ionization cross section of the corresponding ion. This proportionality holds for energies of more than 100 eV above threshold and is explained by an

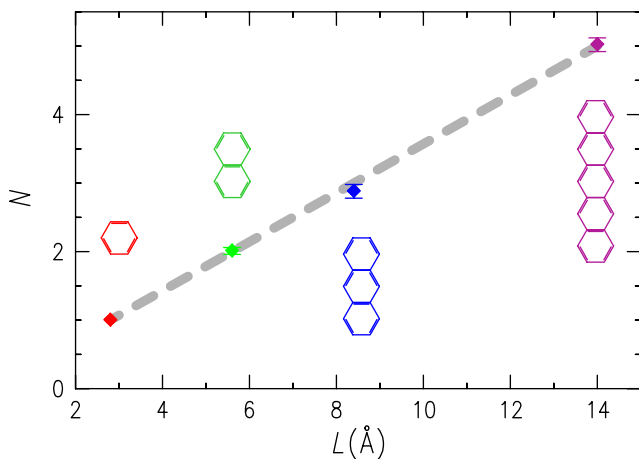


FIG. 3 (color online). The normalization factor  $N$  relative to benzene ( $N = 1$ ) used in Fig. 2 as a function of the length of the molecule for naphthalene, anthracene, and pentacene. The straight dashed line (gray) is to guide the eye.

internal electron-impact process in which the photon-absorbing electron ionizes a second electron by impact [17]. We mention that double photoionization has been observed for helium dimers, where the origins of the two emitted electrons were up to 6 Å apart [33]. Here, we observe the knockout mechanism *directly* for molecules as large as 14 Å without the need to compare the results to electron-impact data.

The gray curve in Fig. 2 is the He double-to-total photoionization ratio [24] normalized to fit our data. Near threshold one can see an almost parabolic onset over 6 eV except for benzene, which has an approximately parabolic increase of the ratio over a much shorter range of about 1.5 eV. However, in all cases the transition is gradual and no distinct boundary for a parabolic increase can be seen. Beyond the near-threshold region the agreement with the He ratio curve is remarkable. To achieve this agreement only the ratio but not the energy axis was scaled. This is another indication that the knockout mechanism is dominant, because it is known from He that this mechanism is dominant at lower energies while the shakeoff process becomes most important at higher energies. Note, however, that the agreement with the He ratio curve does not mean that the molecules studied here are like He. Rather, He is the clearest example for the knockout mechanism. In fact, the shapes of the ratio curves of several other atoms (e.g., Li, Be, Mg) are very similar to the shape of the He ratio curve [32,34,35].

A sketch of the knockout mechanism for anthracene is presented in Fig. 4. When a photon of sufficient energy is absorbed by an electron, the electron can leave the molecule, resulting in single ionization (1), or it can move along the molecule where it has a chance to hit another electron and can cause double ionization (2). If the photon energy is low (but above double-ionization threshold), the first electron is slow and spends more time inside the molecule before leaving and, thus, has a higher probability to knock out a second electron. Therefore, the knockout mechanism is dominant at lower energies.

In summary, we have determined the ratio of doubly charged to all parent ions of partially deuterated benzene,

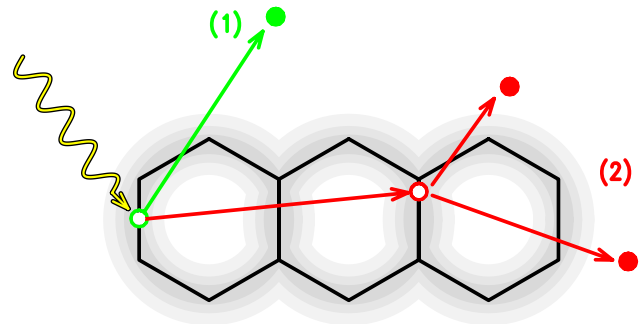


FIG. 4 (color online). Sketch of the double-photoionization mechanism that leads to a length scaling of the ratio  $R_a$ .

naphthalene, anthracene, and pentacene up to 30 eV above their double-ionization thresholds. These ratios increase linearly with the length of the molecule. This means that the general structure (here: the length) of a molecule can have a significant influence on the ratio and that the origin of the two emitted electrons can be as far apart as the length of the molecule; i.e., the double-photoionization process is not a local event. Moreover and quite surprisingly, the overall energy dependences of the molecules' ratios are very similar to that of He. This means that the structure of these molecules does not affect the shape of the energy dependence of the ratio in comparison to the "structureless" He atom. We interpret our observations as direct evidence for the validity of the knockout model even for large molecules and not just for atoms.

We want to mention that the increase of the ratio may not only be valid for molecules of increasing lengths but also for molecules that increase in size in two dimensions such as coronene (a benzene ring surrounded by six benzene rings). While our findings pertain to measurements on benzene and other acenes, we expect this to be a general effect for as long as the molecular ion remains stable after double photoionization. The fact that large molecules can have a relatively high double-photoionization probability leads to a high production of low-energetic electrons that are able to attach to other molecules making them prone to radiation damage. Moreover, large molecules may prove to be a fertile ground for studying structure dependence of the double-photoionization process.

The authors are grateful for assistance by the SRC staff. K. C. and B. R. were supported through the REU program of the National Science Foundation (NSF). This work is based upon research conducted at the Synchrotron Radiation Center, University of Wisconsin—Madison, which was supported by the NSF under Grant No. DMR-0084402.

---

\*Present address: PSI, CH-5232 Villigen, Switzerland

†wehlitz@src.wisc.edu

- [1] P. Bolognesi, G. C. King, and L. Avaldi, *Radiat. Phys. Chem.* **70**, 207 (2004).
- [2] R. Dörner *et al.*, *Phys. Rev. Lett.* **76**, 2654 (1996).
- [3] R. Wehlitz, in *Advances in Atomic, Molecular, and Optical Physics* edited by E. Arimondo, P. R. Berman, and C. C. Lin (Academic Press, New York, 2010), Vol. 58, pp. 1–76.

- [4] M. Stankiewicz *et al.*, *J. Phys. B* **22**, 21 (1989).
- [5] A. P. Hitchcock, J. J. Neville, A. Jürgensen, and R. G. Cavell, *J. Electron Spectrosc. Relat. Phenom.* **88–91**, 71 (1998).
- [6] T. Masuoka, *J. Chem. Phys.* **115**, 264 (2001).
- [7] W. Vanroose, F. Martin, T. N. Resigno, and C. W. McCurdy, *Science* **310**, 1787 (2005).
- [8] M. S. Schöffler *et al.*, *Science* **320**, 920 (2008).
- [9] B. Brehm, U. Fröbe, and H.-P. Neitzke, *Int. J. Mass Spectrom. Ion Process.* **57**, 91 (1984).
- [10] R. I. Hall *et al.*, *Chem. Phys.* **187**, 125 (1994).
- [11] S. Leach, J. H. D. Eland, and S. D. Price, *J. Phys. Chem.* **93**, 7583 (1989).
- [12] R. Wehlitz *et al.*, *Phys. Rev. Lett.* **67**, 3764 (1991).
- [13] B. Boudaïffa, P. Cloutier, D. Hunting, M. A. Huels, and L. Sanche, *Science* **287**, 1658 (2000).
- [14] F. Martin *et al.*, *Phys. Rev. Lett.* **93**, 068101 (2004).
- [15] The C-C distance is 1.399 Å; K. Tamagawa, T. Iijima, and M. Kimura, *J. Mol. Struct.* **30**, 243 (1976).
- [16] R. B. Campbell, J. Monteath Robertson, and J. Trotter, *Acta Crystallogr.* **14**, 705 (1961).
- [17] J. A. R. Samson, *Phys. Rev. Lett.* **65**, 2861 (1990).
- [18] Sigma-Aldrich, 98% purity.
- [19] Alfa-Aesar, 99.6% purity.
- [20] Alfa-Aesar, 99.9% purity.
- [21] Alfa-Aesar, 99.9% purity.
- [22] R. K. Cole *et al.*, *Rev. Sci. Instrum.* **60**, 2093 (1989).
- [23] R. Wehlitz, D. Lukić, C. Koncz, and I. A. Sellin, *Rev. Sci. Instrum.* **73**, 1671 (2002).
- [24] J. A. R. Samson *et al.*, *Phys. Rev. A* **57**, 1906 (1998).
- [25] A. P. Hitchcock and J. J. Neville, in *Chemical Applications of Synchrotron Radiation* edited by T.-K. Sham, Advanced Series in Physical Chemistry Vol. 12A (World Scientific Publishing, Singapore, 2002), pp. 154–227.
- [26] F. H. Dorman and J. D. Morrison, *J. Chem. Phys.* **35**, 575 (1961).
- [27] S. Tobita *et al.*, *Can. J. Phys.* **72**, 1060 (1994).
- [28] M. E. Wacks and V. H. Dibeler, *J. Chem. Phys.* **31**, 1557 (1959).
- [29] J. H. McGuire *et al.*, *J. Phys. B* **28**, 913 (1995).
- [30] T. Pattard and J. Burgdörfer, *Phys. Rev. A* **64**, 042720 (2001).
- [31] T. Schneider, P. L. Chocian, and J.-M. Rost, *Phys. Rev. Lett.* **89**, 073002 (2002).
- [32] R. Wehlitz and S. B. Whitfield, *J. Phys. B* **34**, L719 (2001).
- [33] T. Havermeier *et al.*, *Phys. Rev. Lett.* **104**, 153401 (2010).
- [34] J. B. Bluett, D. Lukić, S. B. Whitfield, and R. Wehlitz, *Nucl. Instrum. Methods Phys. Res., Sect. B* **241**, 114 (2005).
- [35] S. Huotari *et al.*, *Phys. Rev. Lett.* **101**, 043001 (2008).