Chemical Physics Letters 785 (2021) 139144

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Enhanced single-photon double ionization near threshold of substituted benzenes by synchrotron radiation

Tian Sun [a,b], Tianxiang Yang [a,b], Haifeng Xu [a,b,*], Xiangkun Wu [c], Tongpo Yu [c], Xiaoguo Zhou [c,*]

[a] Institute of Atomic and Molecular Physics, Jilin University, Changchun 130012, China
[b] Jilin Provincial Key Laboratory of Applied Atomic and Molecular Spectroscopy, Jilin University, Changchun 130012, China
[c] Hefei National Laboratory for Physical Sciences at the Microscale, Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China

ARTICLE INFO

Keywords:
Single photon double ionization (spDI)
Substituted benzenes
Knock-out
Synchrotron radiation

ABSTRACT

We investigate single photon double ionization (spDI) of substituted benzenes (toluene, chlorobenzene and fluorobenzene) in photon energy of 20–40 eV. We observe that a resonance-like enhancement of spDI, which deviates from the prediction of the "knock-out" mechanism, appears at a specific photon energy near the threshold for halogenated benzenes, but not for toluene. The enhanced spDI occurs if the de Broglie wavelength of the two-electron pseudoparticle matches the size of the conjugated p-*π* orbital of halogenated benzene. Our study shows that the molecular spDI is not a local event and the molecular orbital plays a pivotal role in double ionization.

1. Introduction

Single photon double ionization (spDI), *i.e*, simultaneous removal of two electrons from an atom or molecule with absorption of one photon energy, is a fundamental process to understand the two-electron correlation in atoms and molecules. Atomic spDI has been investigated for a long time for different atoms including helium [1–3], lithium [4,5], and other alkali and alkaline-earth metal atoms [6–9]. It is found that the relative double ionization cross-section, which can be represented by the ratio of the yield of doubly charged ions to that of singly charged ions (M^{2+}/M^{+}), shows a very similar dependence on the photon energy for different kinds of atoms [10]. This fact indicates the common spDI mechanism of atoms, termed as a "knock-out" process in which the photo-absorbing electron knocks out the second electron on its way out [11]. It is now believed that the mechanism of atomic spDI is a "knock-out" process at an excess energy (photon energy minus double ionization threshold) up to 250 eV [3].

Comparing to that of atoms, our knowledge about the spDI of large polyatomic molecules is rather limited. It has been shown that one can qualitatively understand the mechanism of molecular spDI by measuring the energy dependence of the M^{2+}/M^{+} ratio and comparing to the scaled results of He atom [12]. The "knock-out" mechanism as in atomic spDI has been demonstrated to have a significant contribution in spDI for many polyatomic molecules [12]. As already been identified in atoms, the "knock-out" mechanism is also viewed as the "two-step-one'' [1] or the "half-collision'' model [13], which can be explained by an internal electron-impact process in which the photon-absorbing electron ionizes a second electron by impact [14]. For molecules, the "knock-out" mechanism of spDI has been directed observed even for molecules as large as 14 Å [15]. Interestingly, apparent enhancement in spDI over the "knock-out" contribution has been observed at a particular excess energy for benzene and aromatic molecules [12,16] as well as C_{60} molecules [17,18]. Studies on spDI of aromatic molecules have found that the resonance occurs at the excess energy (∼40 eV above the DI threshold) corresponding to the de Broglie wavelength of the two-electron pseudoparticle (λ_{2e}) if it matches the C-C bond distance in the benzene ring [16]. While the underlying physics is not completely understood and requires further investigations, such resonance-like enhancement which deviates from the atomic spDI clearly indicates the effect of the molecular structure in double ionization of polyatomic molecules.

Here, we investigated the spDI of three substituted benzenes (toluene, fluorobenzene and chlorobenzene) using synchrotron radiation, especially near their double ionization thresholds. Apparent enhancement in double ionization has been observed in the spDI of halogenated benzenes at excess energy of 3–4 eV, but is absent in the case of toluene. Analysis indicates that the size and structure of the

---

[*] Corresponding authors at: Institute of Atomic and Molecular Physics, Jilin University, Changchun 130012, China (H. Xu).
E-mail addresses: xuhf@jlu.edu.cn (H. Xu), xzhou@ustc.edu.cn (X. Zhou).

https://doi.org/10.1016/j.cplett.2021.139144
Received 19 August 2021; Received in revised form 12 October 2021; Accepted 13 October 2021

molecular orbitals from which the electrons are removed play a significant role in spDI of polyatomic molecules.

2. Experiment

The experiment was performed at the BL09U beamline of the National Synchrotron Radiation Laboratory in Hefei, China [19]. The synchrotron radiation emitted from an undulator was dispersed by a 6 m grating monochromator equipped with a 740 lines/mm spherical grating [20], which covers the energy range of 15–45 eV photons. When the entrance and exit slits are fixed at 80 μm, the photon energy resolution (ΔE/E) is about 1.1×10^{-4} (at a photon energy of 25 eV). By comparing the photoionization efficiency curve of inert gas (He), the photon energy was calibrated with less than ± 5 meV error. A silicon photodiode (SXUV-100, International Radiation Detections, Inc) was used to measure photon flux and normalize the collected signal.

A refletron time-of-flight mass spectrometer was used to measure the ion yields, which has been described in detail in previous studies [21,22]. Briefly, toluene, fluorobenzene (both at room temperature) and chlorobenzene (heated in a water bath at 60 °C) molecules carried by the carrier gas (Ar, the stagnation pressure of 1.2 atm) were introduced into the vacuum chamber via a 30 μm-diameter nozzle and a skimmer to form a supersonic molecular beam. The molecular beam interacted with the synchrotron radiation to generate ions in the ionization chamber, which were extracted and finally collected by a refletron time-of-flight mass spectrometer with MCP detectors. The MCP detector was operated with 3000 V bias voltage, which can ensure an approximately uniform detection efficiency for all ions independent of their mass-to-charge ratio [23]. A counter (Multiscaler P7888, Fast Com Tek, Germany) was used to record relative flying time of every ion. The working pressures of the source chamber and the ionization chamber of the refletron time-of-flight mass spectrometer were 4×10^{-2} Pa and 2×10^{-5} Pa, respectively.

3. Results and discussion

3.1. Double ionization threshold

Using time-of-flight (ToF) mass spectroscopy, we have measured ionic yields of three substituted-benzene molecules (toluene, fluorobenzene and chlorobenzene) ionized by the synchrotron radiation at the photon energies from 20 to 40 eV. Doubly-charged parent ion (M^{2+}) of each molecule appears as the photon energy is higher than 24 eV. To determine the double ionization threshold (IE_2), we present in Fig. 1 (a) (b) and (c) the ratios of doubly to singly charged parent ions (M^{2+}/M^{+}) as a function of photon energy, for toluene, fluorobenzene and chlorobenzene, respectively. The IE_2 value of each substituted-benzene can be determined by fitting the measured M^{2+}/M^{+} results using the empirical method according to [12]:

$$M^{2+}/M^{+}(h\nu) = a \times (h\nu - IE_2)^n + b \tag{1}$$

where $h\nu$ is the photon energy, a is a fit parameter, n is an exponent and b is an additional offset. As shown in Fig. 1, our results can be well fitted with the above empirical equation, and the IE_2 values obtained from the fitting are listed in Table 1. We have also performed calculations on the IE_2 values of the substituted-benzenes, using Density Functional Theory (DFT) method at the B3LYP/6-311G (d,p) level. The calculation results are in relatively good agreement with the experimental measurement (see Table 1). The double ionization thresholds of fluorobenzene and toluene have been measured in the literature [24,25], and the deviations between our results and those reported previously are 0.23 eV for fluorobenzene and only 0.014 eV for toluene.

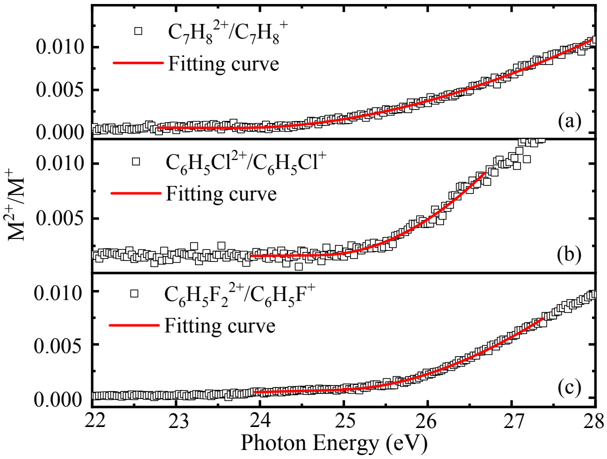

Fig. 1. Measured ratio of M^{2+}/M^{+} for toluene, chlorobenzene and fluorobenzene (open squares) near threshold. The red line indicates the fitting result of least squares method. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In these three substituted benzenes, the IE_2 values of halogenated benzenes (chlorobenzene and fluorobenzene) are close and are about 1 eV higher than that of toluene. We also note that the threshold of each substituted benzene is lower than that of benzene ($IE_2 = 26.1$ eV) [26]. For organic molecules, Eland [27] proposed an empirical rule concerning the relationship of IE_2 and single ionization threshold (IE_1), i.e., $IE_2 = 2.8(\pm 0.1) \times IE_1$. The ratio of IE_2/IE_1 of each substituted benzene lies at above 2.7, which is in good accordance to Eland's empirical rule.

3.2. Enhanced single photon double ionization near the threshold

It is well known that the mechanism of atomic spDI is a "knock-out" [11] process at low excess energy ($h\nu - IE_2$) (For atom He, spDI is a "knock-out" process when the excess energy is below 250 eV [3]). For polyatomic molecules, by comparing the M^{2+}/M^{+} ratio curve (i.e., dependence of the ratio on the excess energy) with the scaled M^{2+}/M^{+} curve of He, one may understand the contribution of "knock-out" mechanism to spDI [12]. Fig. 2 shows the M^{2+}/M^{+} curves of toluene, chlorobenzene and fluorobenzene in the excess energy of 0–16 eV. The solid lines in the figure represent the scaled ratio of He (i.e., $N \times (He^{2+}/He^{+})$, where N is the scaling factor and He^{2+}/He^{+} results are obtained from ref. [3]). For reference, the original results of He^{2+}/He^{+} [3] are also presented in the figure (dashed line). The scaling factor N of toluene, chlorobenzene and fluorobenzene are 2.5, 6.8 and 3.2, respectively. As one can see from the figure, the M^{2+}/M^{+} curve of each molecule generally agrees with the scaled result of He. This consistence indicates that spDI of the substituted benzenes investigated in the study is also a "knock-out" process, which is in accordance with the results of benzene [12] and various benzene derivatives [16] as well as heterocyclic molecules [12,16,31,32]. It should be noted that only the He^{2+}/He^{+} ratio but not the excess energy axis is scaled to achieve the agreement with the results of molecules, since the knockout mechanism is dominant at

Table 1
Ionization thresholds of the substituted-benzenes (in unit of eV).

Sample	IE_2		IE_1	IE_2/IE_1
	This work	Ref.		
C_7H_8	23.82[a]/23.33[b]	23.81[c]	8.83 ± 0.001[e]	2.70
C_6H_5Cl	24.73[a]/24.86[b]		9.07 ± 0.02[f]	2.73
C_6H_5F	24.97[a]/24.69[b]	25.20[d]	9.20 ± 0.01[g]	2.71

[a] Experimental results.
[b] DFT Calculation results.
[c] Roithová [25].
[d] Griffiths [24].
[e] Lu [28].
[f] Baer [29].
[g] Watanabe[30].

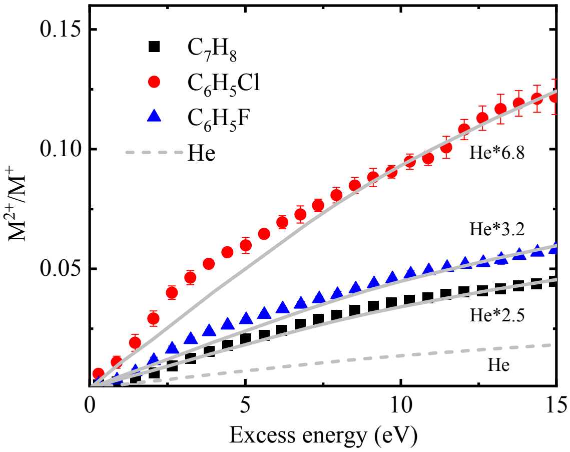

Fig. 2. Ratio of the doubly to singly charged parent ions of toluene (black square), chlorobenzene (red circle), fluorobenzene (blue triangle). The solid lines represent the scaled ratio of He (i.e., $N\times(He^{2+}/He^{+})$, where N is the scaling factor and He^{2+}/He^{+} results are obtained from ref. [3]). The dashed line represent the original results of He^{2+}/He^{+} [3]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

low photon energies while the shakeoff process becomes more significant at higher energies [15].

It is interesting to find that the ratio M^{2+}/M^{+} of chlorobenzene or fluorobenzene deviates from the prediction of the "knock-out" mechanism near the threshold, which is significantly higher than the scaled results of He at the excess energy of 3–5 eV. Such enhancement of spDI is not observed in the case of toluene, where the ratio M^{2+}/M^{+} of which agrees well with the scaled results of He in the whole range of the photon energy in the study. This observation can be seen more clearly if one subtracts the knock-out contribution ($K = N\times(He^{2+}/He^{+})$, i.e., the solid line in Fig. 2) from the measured ratios. As shown in Fig. 3, a clear hump structure appears in the results of chlorobenzene and fluorobenzene with the peak centered at the excess energy of 3.7 and 4.4 eV, respectively, while no such structure is observed in the result of toluene.

The apparent deviation from the "knock-out" mechanism as in atoms indicates that the molecular structure effect plays a significant role in spDI of polyatomic molecules. While having not been observed near the double ionization threshold, similar hump structure to that in Fig. 3 has been observed in the literatures at an excess energy around 40 eV for spDI of several aromatic molecules including naphthalene, anthracene and deuterated benzene [12,16]. To understand this phenomenon, the electrons released from a molecule are treated as a two-electron pseudoparticle. The de Briglie wavelength of a two-electron pseudo-particle can be calculated:

$$\lambda_{2e} = \frac{h}{P_{2e}} = \frac{h}{\sqrt{2mE}} \tag{2}$$

where λ_{2e} is the de Broglie wavelength of the two-electron pseudo-particle, h is the Planck constant, P_{2e} is the momentum, m is the mass of two electrons ($m = 2m_e$), E is the energy. It is pointed out that if λ_{2e} equals to the C-C bond distance in the benzene ring (~1.4 Å), the de Broglie wave will form a standing wave in the π orbital of the molecule, leading to a resonance effect that enhances the probability of double ionization at a particular excess energy ($\lambda_{2e} = 1.4$ Å, the corresponding energy is at 38.4 eV which is close to the resonance energy in spDI of aromatic molecules). In our study, however, the resonance appears at small excess energies of 3.7 and 4.4 eV, corresponding to λ_{2e} of 4.5 and 4.1 Å for chlorobenzene and fluorobenzene respectively. The corresponding λ_{2e} values are 2–4 times longer than any of the bond lengths of the molecules (see Fig. 4 for the geometric structures of the molecules). On the other hand, the λ_{2e} values in the present study are surprisingly close to the distance between the halogen atom and the carbon atom at the para position of the benzene ring ($L_{CCl} = \sim 4.53$ Å for chlorobenzene and $L_{CF} = \sim 4.13$ Å for fluorobenzene). This indicates that the enhancement in spDI near the threshold is related to the size of the molecule, or the size of the conjugated p-π orbital of halogenated benzene as we will discuss below.

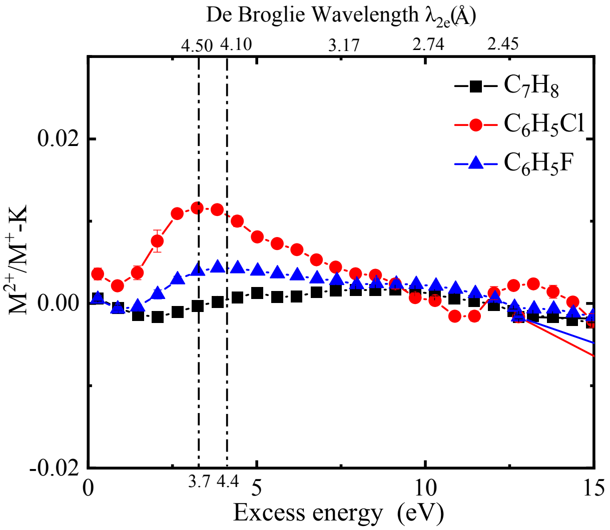

Fig. 3. Ratio of M^{2+}/M^{+} for toluene (black square), chlorobenzene (red circle), and fluorobenzene (blue triangle) after subtracting the knock-out contribution K (M^{2+}/M^{+} - K). The upper axis shows the de Broglie wavelength of a two-electron pseudoparticle. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The fact that the enhancement is much less significant in the result of toluene than those of halogenated benzenes is another indication about the molecular orbital effect in spDI. For spDI, two electrons in a molecule are removed from the highest occupied molecular orbital (HOMO). The HOMOs of the three substituted benzenes are presented in Fig. 4. For a halogenated benzene, the p orbital of the halogenated atom and the π orbital of the benzene ring form a delocalized conjugated p-π orbital. The HOMO of toluene is hyperconjugation, which is formed by the σ orbital of the C atom in methyl group and the π orbital of the benzene ring. Comparing to conjugated p-π orbital in halogenated benzenes, the hyperconjugated σ-π orbital in toluene is less delocalized. Our results indicate that the double ionization process can take place involving two atoms which are correlated by a delocalized electronic orbital and can be as far apart as > 4 Å if the de Broglie wavelength matches the distance between them. This leads to enhanced spDI at the corresponding energy, as we have observed in the study. Our study confirms that the double ionization process is not a local event, or more precisely, two electrons can be emitted as far apart as the size of the delocalized electronic orbital of a molecule.

4. Conclusion

In summary, we investigated the influence of the molecular structure on spDI of substituted benzenes at the photon energy of 20–40 eV using synchrotron radiation. The ratio of doubly to singly charged parent ions of each substituted benzene is measured as a function of photon energy, and is compared with the results of the scaled He atom. While the mechanism could be viewed as a "knock-out" process, it is interesting to find different behaviors of spDI between halogenated benzenes and toluene. A resonance-like enhancement of the double ionization yield, which deviates from the prediction of the "knock-out" mechanism, appears at a specific photon energy near the threshold for halogenated benzenes, but is not apparent in the case of toluene. It is indicated that

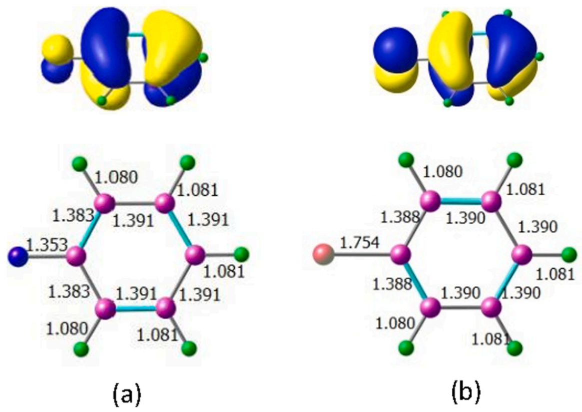

Fig. 4. Highest Occupied Molecular Orbitals (HOMOs, upper panel) and molecular geometric structure (lower panel) of the substituted benzenes, (a) fluorobenzene, (b) chlorobenzene and (c) toluene. Bond lengths are in unit of angstrom.

such enhanced spDI occurs if the de Broglie wavelength of the two-electron pseudoparticle matches the size of the conjugated p-π orbital of halogenated benzene. Our study confirms the significant influence of the molecular orbital structure on the double ionization of polyatomic molecules.

CRediT authorship contribution statement

Tian Sun: Investigation, Writing – original draft. **Tianxiang Yang:** Investigation, Formal analysis. **Haifeng Xu:** Supervision, Writing – review & editing. **Xiangkun Wu:** Formal analysis. **Tongpo Yu:** Data curation. **Xiaoguo Zhou:** Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

This work was financially supported by the National Natural Science Foundation of China (No. 21903079, 21873089, 11874179). X. Zhou also thanks the USTC-NSRL Association for financial support.

References

[1] J.H. McGuire, N. Berrah, R.J. Bartlett, J.A.R. Samson, J.A. Tanis, C.L. Cocke, A. S. Schlachter, The ratio of cross sections for double to single ionization of helium by high energy photons and charged particles, J. Phys. B: At. Mol. Opt. Phys. 28 (6) (1995) 913–940.

[2] R. Dörner, T. Vogt, V. Mergel, H. Khemliche, S. Kravis, C.L. Cocke, J. Ullrich, M. Unverzagt, L. Spielberger, M. Damrau, O. Jagutzki, I. Ali, B. Weaver, K. Ullmann, C.C. Hsu, M. Jung, E.P. Kanter, B. Sonntag, M.H. Prior, E. Rotenberg, J. Denlinger, T. Warwick, S.T. Manson, H. Schmidt-Böcking, Ratio of Cross Sections for Double to Single Ionization of He by 85–400 eV Photons, Phys. Rev. Lett. 76 (15) (1996) 2654–2657.

[3] J.A.R. Samson, W.C. Stolte, Z.-X. He, J.N. Cutler, Y. Lu, R.J. Bartlett, Double photoionization of helium, Phys. Rev. A 57 (3) (1998) 1906–1911.

[4] R. Wehlitz, J.B. Bluett, S.B. Whitfield, Oscillations in the Double-Photoionization Cross Section of Li near Threshold, Phys. Rev. Lett. 89 (9) (2002), 093002.

[5] M.-T. Huang, R. Wehlitz, Y. Azuma, L. Pibida, I.A. Sellin, J.W. Cooper, M. Koide, H. Ishijima, T. Nagata, Single and double photoionization of lithium, Phys. Rev. A 59 (5) (1999) 3397–3401.

[6] D. Lukić, J.B. Bluett, R. Wehlitz, Unexpected Behavior of the Near-Threshold Double-Photoionization Cross Section of Beryllium, Phys. Rev. Lett. 93 (2) (2004), 023003.

[7] P.N. Juranić, J. Nordberg, R. Wehlitz, Single- and double-photoionization data of Na and K corroborate the existence of a universal scaling law for the ratio, Phys. Rev. A 74 (4) (2006), 042707.

[8] F.J. Wuilleumier, L. Journel, B. Rouvellou, D. Cubaynes, J.M. Bizau, Z. Liu, J. Liu, M. Richter, P. Sladeczek, K.H. Selbman, P. Zimmermann, Direct Double Photoionization Involving Inner and Outer Electrons: First Experimental Determination and Many-Body Calculations of an Absolute Cross Section, Phys. Rev. Lett. 73 (23) (1994) 3074–3077.

[9] R. Wehlitz, P.N. Juranić, D.V. Lukić, Double photoionization of magnesium from threshold to 54 eV photon energy, Phys. Rev. A 78 (3) (2008), 033428.

[10] R. Wehlitz, Chapter 1 - Simultaneous Emission of Multiple Electrons from Atoms and Molecules Using Synchrotron Radiation, in: Advances In Atomic, Molecular, and Optical Physics, 58, Academic Press, 2010, pp. 1–76.

[11] T. Schneider, P.L. Chocian, J.-M. Rost, Separation and Identification of Dominant Mechanisms in Double Photoionization, Phys. Rev. Lett. 89 (7) (2002), 073002.

[12] T. Hartman, P.N. Juranić, K. Collins, B. Reilly, E. Makoutz, N. Appathurai, R. Wehlitz, Photo-double-ionization mechanisms in aromatic hydrocarbons, Phys. Rev. A 87 (6) (2013), https://doi.org/10.1103/PhysRevA.87.063403.

[13] T. Pattard, J. Burgdörfer, Half-collision model for multiple ionization by photon impact, Phys. Rev. A 64 (4) (2001), 042720.

[14] J.A.R. Samson, Proportionality of electron-impact ionization to double photoionization, Phys. Rev. Lett. 65 (23) (1990) 2861–2864.

[15] T. Hartman, P.N. Juranić, K. Collins, B. Reilly, N. Appathurai, R. Wehlitz, Large Molecules Reveal a Linear Length Scaling for Double Photoionization, Phys. Rev. Lett. 108 (2) (2012), https://doi.org/10.1103/PhysRevLett.108.023001.

[16] R. Wehlitz, P.N. Juranić, K. Collins, B. Reilly, E. Makoutz, T. Hartman, N. Appathurai, S.B. Whitfield, Photoemission of cooper pairs from aromatic hydrocarbons, Phys Rev Lett 109 (19) (2012), https://doi.org/10.1103/PhysRevLett.109.193001.

[17] P.N. Juranić, D. Lukić, K. Barger, et al., Experimental Evidence for Modulations in the Relative Double-Photoionization Cross Section of C$_{60}$ from Threshold up to 280 eV, Phys. Rev. Lett. 96 (2) (2006), 023001.

[18] P.N. Juranić, D. Lukić, K. Barger, et al., Multiple photoionization and fragmentation of C$_{60}$ in the 18–280 eV range, Phys. Rev. A 73 (4) (2006), 042701.

[19] S. Wang, R. Kong, X. Shan, Y. Zhang, L. Sheng, Z. Wang, L. Hao, S. Zhou, Performance of the atomic and molecular physics beamline at the National Synchrotron Radiation Laboratory, J. Synchrotron Radiat. 13 (6) (2006) 415–420.

[20] C.T. Chen, Concept and design procedure for cylindrical element monochromators for synchrotron radiation, Nucl. Instrum. Methods Phys. Res., Sect. A 256 (3) (1987) 595–604.

[21] W. Fang, G. Lei, X. Shan, F. Liu, Z. Wang, L. Sheng, A VUV photoionization organic aerosol mass spectrometric study with synchrotron radiation, J. Electron Spectrosc. Relat. Phenom. 184 (3-6) (2011) 129–133.

[22] Q. Zhang, W. Fang, Y. Xie, M. Cao, Y. Zhao, X. Shan, F. Liu, Z. Wang, L. Sheng, Photoionization and dissociation study of p-nitrotoluene: Experimental and theoretical insights, J. Mol. Struct. 1020 (2012) 105–111.

[23] H.C. Straub, M.A. Mangan, B.G. Lindsay, K.A. Smith, R.F. Stebbings, Absolute detection efficiency of a microchannel plate detector for kilo-electron volt energy ions, Rev. Sci. Instrum. 70 (11) (1999) 4238–4240.

[24] W.J. Griffiths, M.L. Langford, F.M. Harris, Double-ionization energies of fluorinated benzene molecules, J. Am. Soc. Mass Spectrom. 4 (6) (1993) 513–518.

[25] J. Roithová, D. Schröder, J. Loos, H. Schwarz, H.-C. Jankowiak, R. Berger, R. Thissen, O. Dutuit, Revision of the second ionization energy of toluene, J. Chem. Phys. 122 (9) (2005) 094306, https://doi.org/10.1063/1.1856916.

[26] F.H. Dorman, J.D. Morrison, Double and Triple Ionization in Molecules Induced by Electron Impact, J. Chem. Phys. 35 (2) (1961) 575–581.

[27] B.P. Tsai, J.H.D. Eland, Mass spectra and doubly charged ions in photoionization at 30.4 nm and 58.4 nm, Int. J. Mass Spectrom. Ion Phys. 36 (2) (1980) 143–165.

[28] K.T. Lu, G.C. Eiden, J.C. Weisshaar, Toluene cation: nearly free rotation of the methyl group, J. Phys. Chem. 96 (24) (1992) 9742–9748.

[29] T. Baer, B.P. Tsai, D. Smith, et al., Absolute unimolecular decay rates of energy selected metastable halobenzene ions, J. Chem. Phys. 64 (6) (1976) 2460–2465.

[30] K. Watanabe, T. Nakayama, J. Mottl, Ionization potentials of some molecules, J. Quant. Spectrosc. Radiat. Transfer 2 (4) (1962) 369–382.

[31] T. Hartman, R. Wehlitz, Role of the nitrogen atom in double photoionization of monocyclic hydrocarbons, Phys. Rev. A 91 (6) (2015), https://doi.org/10.1103/PhysRevA.91.063419.

[32] R. Wehlitz, T. Hartman, Double photoionization of thiophene, J. Phys. Conf. Ser. 493 (2014) 012002, https://doi.org/10.1088/1742-6596/493/1/012002.