Double Photoionization in Ring Molecules: Search of the Cooper Pair Formation

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We provide a final state selective experimental study on the direct double photoionization of the valence states of benzene and pyrrole. The experiment is carried out using a magnetic-bottle electron time-of-flight coincidence setup at the incident photon energy region of 25–120 eV. We discuss on the recently discovered phenomenon of so-called Cooper pair formation [R. Wehlitz *et al.*, Phys. Rev. Lett. **109**, 193001 (2012)] and show that our experiment provides contradicting evidence on its existence in the proposed form. We confirm the finding of a new two-electron continuum resonance structure observed at about 30–70 eV above the double ionization threshold in benzene, provide further information from it, and suggest an alternative explanation.

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Double photoionization (DPI) is a phenomenon where single photon absorption releases two electrons into the continuum from a bound system that can be in atomic, molecular, or solid phase. DPI divides into direct and indirect processes. Direct DPI is simultaneous emission of two electrons, whereas indirect DPI is sequential emission of the electrons through the formation of an excited, singly charged intermediate state. Direct DPI processes have been studied extensively in atoms and are nowadays fairly well understood in small symmetric systems (see, e.g., Refs. [1–3] and references therein). Because of the developments in experimental techniques, research on direct DPI has been recently extended to molecular samples leading to fascinating studies, such as two-site double core ionization [4], hollow molecules [5], DPI over a distance of 10 Å in He_2 [6], and observation of double slitlike interference in H_2 [7].

Direct DPI in weak photon fields arises from electron correlation and is often divided into two mechanisms that are called *shakeoff* arising from the sudden collapse of the bound orbitals and *knockout* coming from the (virtual) inelastic collision between the first and second electron [1]. These mechanisms allow the two electrons to divide the excess energy continuously. The energy sharing probability between the electrons is, however, not uniform, but more like U-shaped, where one of the two electrons takes most of the released energy. Because of the continuous energy sharing, DPI can be directly studied only by detecting the two emitted electrons in coincidence. Alternatively, information from DPI can be obtained by detecting the residual ion(s).

The idea of observing a two-electron resonance in molecules that has a mechanism analogous to Cooper pairing in solid lattices is very intriguing as it would provide a new medium for studies of superconductivity. Such studies would have a possibility to shed light on the behavior of superconductivity in the nanometer scale, as well as help to understand the mechanisms behind the high-T_c superconducting materials.

In a recent Letter and its follow-up papers Wehlitz and co-workers [8–10] studied the DPI process in aromatic hydrocarbons using (noncoincident) ion and electron spectroscopies. They discovered that the ratio between doubly and singly charged parent ions produced by DPI in benzene, and polycyclic hydrocarbons naphthalene, anthracene, and coronene show a hitherto unseen "hump" (i.e., sudden rise of intensity) at the energy region about 30–70 eV above the first double ionization threshold. In contrast, the hump was not seen in the pentagonal-shaped molecules pyrrole and furan. The hump was explained by introducing a new DPI mechanism, the so-called Cooper pair formation. The idea behind the mechanism is that at the energy of the hump, the two valence electrons are excited into a quasistable geometrical resonance where the de Broglie wavelength of the excited electron pair is able to form a closed loop standing wave around the molecule. The state is expected to manifest itself by decaying so that the two electrons share the excess energy equally in the molecular frame. The idea was further justified by finding two new peaks in the background of the standard one-electron photoelectron spectrum (PES) recorded from the studied molecules. The finding of two peaks, instead of one corresponding to equal energy share, was explained to be caused by molecular to laboratory frame transformation.

In this Letter we provide the results of an electron-electron coincidence experiment of the valence DPI of benzene (C_6H_6) and pyrrole (C_4H_5N) at the photon energy region of 25–120 eV. The plan of the experiment was to study the new resonance phenomenon final state selectively for the first time by directly detecting the two emitted electrons from Cooper pairs in coincidence. Benzene and pyrrole were chosen because they are the simplest known molecules that should show and not show the new resonance. The reason why benzene shows the hump has been argued [8] to be caused by proper symmetric arrangement of the carbon atoms, which is broken in pyrrole due to the presence of one nitrogen atom in the ring.

As results, we confirm the finding of the new resonance in benzene, and that the resonance seems to be connected to nondissociating dicationic final states. However, our experiment does not support the existence of Cooper pair formation as proposed in Ref. [8]. In addition, energy resolved relative DPI cross sections of benzene and pyrrole that have importance in understanding DPI phenomenon in larger molecules are provided.

The measurements were carried out at the PLEIADES beam line [11,12] of the 2.75 GeV synchrotron storage ring SOLEIL in St Aubin, France. The experiment was done using a magnetic-bottle time-of-flight spectrometer described in detail in Ref. [13]. Briefly, the combination of a strong (0.7 T) and inhomogeneous magnetic field from a permanent magnet near the ionization volume and a weak (1 mT) and uniform magnetic field of a 2 m long solenoid collects essentially all electrons from the ionization volume and guides them onto a microchannel plate detector at the end of the solenoid. A multihit time-to-digital converter measures the arrival time of the electrons with respect to the synchrotron ring clock. SOLEIL synchrotron was operated in the single bunch mode, providing light bunches every 1.184 μs. A mechanical chopper was used to reduce the light pulse period to $\sim$12 μs in order to allow measurement of the absolute time of flight of electrons [13]. The spectrometer had an energy resolution of $\Delta E/E = 1.6\%$ and a detection efficiency of $\sim$70% for electrons of less than 100 eV kinetic energy, as deduced from the comparison of Ar^+ $2p^{-1}$ Auger spectra measured with and without coincidence with the $2p$ photoelectron.

We begin the discussion with Fig. 1, which presents the valence DPI spectrum of benzene and pyrrole at a photon energy of 54 eV. The benzene spectrum in Fig. 1(a) also shows theoretical calculation from the photon energy independent Green's function method from Ref. [14]. The experimental DPI spectrum of benzene has been discussed before by Eland [15] and the spectrum in Fig. 1(a) agrees well with the results presented in Ref. [15]. To our knowledge the valence DPI electron spectrum of pyrrole has not been studied before. The spectra are constructed by summing over all electron pairs fulfilling the relation $h\nu - E_b^{2+} = E_{k_1} + E_{k_2}$, where E_b^{2+} is the double ionization threshold and E_{k_i} are the kinetic energies of the emitted electrons. The summation includes the contributions from both direct and indirect DPI processes, as discussed, e.g., in Ref. [15].

Both spectra show discrete structures at the region of the first doubly ionized states and a continuous slowly decreasing structure at higher energies, which is caused by the large number of unresolved dicationic final states. In the following, we concentrate on the three resolved structures in benzene and five in pyrrole which are indicated in Fig. 1. Note that these structures do not represent individual ionic final states. According to Ref. [14], the structures marked Bz1, Bz2, and Bz3 of benzene already contain 3, 7, and 25 final ionic states, respectively, and we may assume similar numbers for pyrrole.

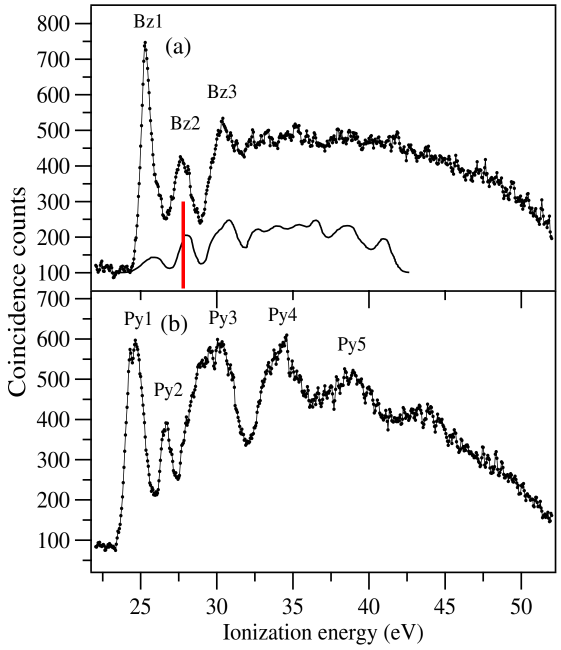

FIG. 1 (color online). Double photoioinization spectrum of (a) benzene and (b) pyrrole recorded at 54 eV photon energy. The spectra show the number of coincidence counts as a function of two-electron binding energy. The red vertical bar in (a) marks the dissociation threshold of dicationic benzene from Ref. [16] and the solid line shows DPI calculation for the first 226 dicationic states from Ref. [14].

Figures 2 and 3 provide relative, detection efficiency corrected, DPI cross sections of benzene and pyrrole as a function of photon energy. Panels 2(a) and 3(a) show the relative total DPI cross section, obtained by dividing the DPI counts by the sum of single photoionization and DPI events at each photon energy. The same panels also present the ion spectroscopic data from Ref. [8] (intensity axis on the right-hand side), but we emphasize that these curves are not directly comparable. This is because the ion spectroscopic graph was obtained by dividing the observed doubly charged parent molecules by all parent molecules. The experiment in Ref. [8] thus does not account for the cross section energy dependence of doubly and singly ionized final states that dissociate prior to detection. According to Ref. [16], dicationic states of benzene higher than 3.15 eV above the double ionization threshold start to dissociate into two singly charged fragments [see the bar

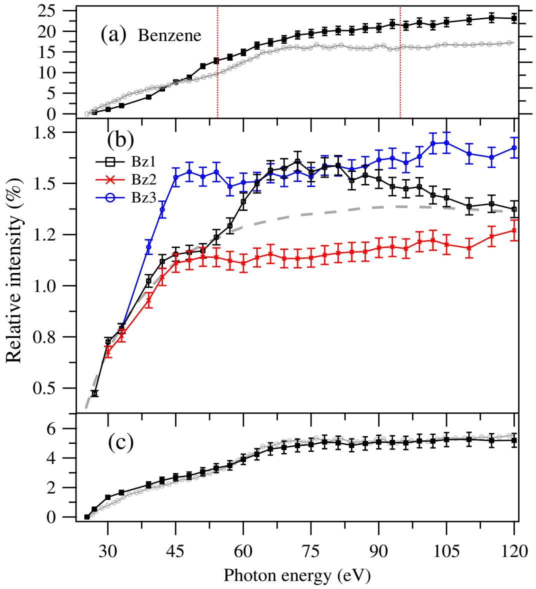

FIG. 2 (color online). Relative DPI probabilities of benzene as a function of photon energy. Black squares in (a) show the total DPI probability obtained from the present data and the gray open circles (scale on the right-hand axis) show ion spectroscopic measurement from Ref. [8]. Lines in (b) depict the partial DPI probabilities of peaks marked in Fig. 1. Dashed gray curve in (b) is scaled DPI probabilities of atomic He from Ref. [18]. Black squares in (c) depict the double-to-single and double ionization ratio from counts corresponding to ionization to nondissociating final states. To help with the comparison, the curve in (c) is scaled to the gray open circles showing the ion spectroscopic measurement.

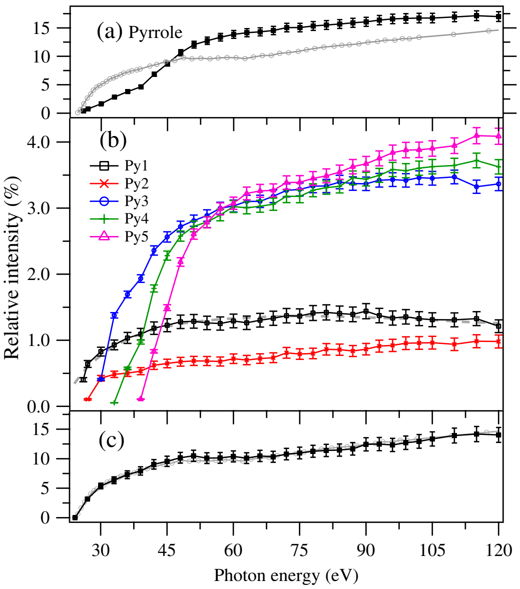

FIG. 3 (color online). Relative DPI probabilities of pyrrole as a function of photon energy. The description of the panels is the same as in Fig. 2.

in Fig. 1(a)]. For dicationic pyrrole, such experimental data are not available, except for studies showing a linear increase of the production of doubly charged parent molecule in the region of a few eV above the double ionization threshold [9,17].

Examining the shape of the total DPI curve in Fig. 2(a) reveals that our *e-e* coincidence data do not show the hump seen in the ion data at the photon energy region of 55–95 eV (between the red dashed vertical lines). This can be explained via the aforementioned enhanced sensitivity of the ion data to stable doubly ionized products. This is indeed the case, as will be shown below.

Figures 2(b) and 3(b) give the partial DPI cross sections of the structures marked in Fig. 1, showing an interesting result. The partial DPI curve of peak Bz1 has a distinct increase of counts at exactly the photon energy region of the hump observed in the ion data in Fig. 2(a). In contrast, such an increase is not present in the partial DPI curves of peaks Bz2 and Bz3, nor in any of the partial DPI curves of pyrrole in Fig. 3(b). There is a difference between the states in Bz1 and Bz2 or Bz3, which is the dissociation. According to Refs. [16,19], the dicationic levels of peak Bz1 do not dissociate the molecule, whereas levels in Bz2 and Bz3 lead to five different combinations of two singly ionized fragments. We may thus assume that this difference is connected to the reason why the ion data show the hump as our Bz1 line. In fact, the hump in the ion has to arise from the first dicationic states, because if all dicationic states would be (meta)stable and if the cross section of all of them would increase at excess energy of about 30–70 eV above their corresponding double ionization thresholds, no hump should be seen due to smearing out by the tens of eV wide band of these states.

This statement becomes evident from Fig. 2(c), which shows the data in a way that the DPI spectrum in Fig. 1(a) is integrated including only stable dicationic final states [i.e., up to the red line in Fig. 1(a)], and normalized using the counts corresponding to ionization to stable singly ionized final states, that are roughly 4.5 eV [20] above the first ionization threshold. In this way the *e-e* coincidence data are expected to yield the same information as the ion data. The obtained curve indeed shows a remarkably good agreement with the ion data, as seen in Fig. 2(c).

The present experiment also reveals that smearing out is, however, not the reason why the hump is missing in the ion spectroscopic data of pyrrole. If the hump is smeared out, it would be present in the final state resolved direct DPI curves in Fig. 3(b), which do not show any unexpected increase of counts. For pyrrole the exact dissociation threshold of dicationic final states is not known. Therefore, the graph in Fig. 3(c) was obtained by integrating over peaks Py1 and Py2, which we assumed to consist of only nondissociating final states. Normalization of the curve was done with the counts corresponding to ionization to singly ionized final states up to 4.1 eV [17] above the first ionization threshold. As for benzene, Fig. 3(c) shows a very good agreement between the electron and ion data. Note that if peak Py3 is included in the generation of the graph in Fig. 3(c), the shape of the curve starts to immediately deviate from the ion data. This result can thus be used to estimate that the dicationic dissociation threshold of pyrrole is roughly about 3.8 eV above the double ionization threshold.

The discussion above proves that there is indeed a difference in the final states of peak Bz1 that is not present in Bz2 or Bz3 nor in pyrrole. Therefore, it is the most prominent candidate showing evidence of Cooper pair formation in double photoionization. Figure 4 depicts a further analysis done for structure Bz1, which are the energy sharing profiles of coincidence electrons at a few selected photon energies. The profiles are formed by subtracting the kinetic energies of the faster electron from the slower electron of a coincidence electron pair, within the excess energy window of Bz1. Because the coincidences are detected using a single detector, coincidences where the two electrons arrive at exactly the same energy cannot be observed. This 5 ns detector dead time leads, however, to a blind window of less than ~400 meV at the photon energy of the resonance.

These plots should unambiguously show the existence of Cooper pair formation, because the pairs should appear as distinct bumps in otherwise smooth curves at the photon energy region of the hump in Fig. 2(b). The red arrows mark the positions where the signal from Cooper pairs (in the laboratory frame) is expected to appear according to the graph plotted in Fig. 4 of Ref. [8], which depict the positions of the two peaks identified to arise from the decay of Cooper pairs as a function of photon energy. The position of the arrows is defined by the kinetic energy difference (at each photon energy) of the two peaks observed in the low kinetic energy background of non-coincident one-electron PES in Ref. [8]. If these peaks would arise from the decay of Cooper pairs, our experiment should show coincidences so that the energy difference of the *e*-*e* pairs equals the energy difference of the observed two peaks in Ref. [8]. As is clear from the figure, we observe no statistically significant increase supporting the existence of Cooper pair formation, not at the expected positions from Ref. [8] nor at (near) equal energy sharing (zero of the x axis in the graph). This demonstrates that, according to our *e*-*e* coincidence experiment, the Cooper pair formation in DPI of ring-shaped hydrocarbons does not exist in the proposed form.

We note that analysis of a high statistics one-electron PES recorded at 75 eV photon energy indeed depicts bumps at 10 and 30 eV kinetic energy, as discussed and identified as evidence of Cooper pair formation in Fig. 3 of Ref. [8]. However, the coincidence data in the graphs of Fig. 4 show clearly that the bumps do not come from electron pairs of the same ionization event. It is left for future studies to find the reason for the two bumps in the data of Ref. [8]. We have also compared the *e*-*e* coincidence maps of the Bz1 peak on and off the resonance. This analysis showed that the increase of *e*-*e* coincidences at the resonance appears to be global, which indicates that the resonance does not arise from an indirect DPI process.

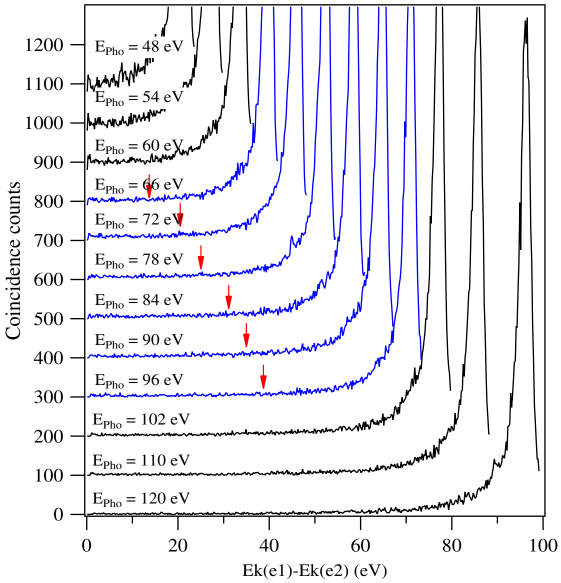

FIG. 4 (color online). Kinetic energy sharing profiles of two electrons emitted in double photoionization to levels in benzene peak Bz1 at few photon energies. Baselines of the profiles are lifted for visibility. The profiles recorded at photon energies 66–96 eV that should show coincidences emitted from Cooper pairs are highlighted in blue, and the red vertical arrows mark the expected positions of the pairs in the laboratory frame from Ref. [8].

As a final remark, we propose that the hump observed in the present study and in Ref. [8] could be a two-electron equivalent to the observed variations in the normal valence PES of C_{60} [21] and C_{70} [22] and the NEXAFS-like oscillations in the 1*s* ionization of benzene [23]. The oscillations in C_{60} and C_{70} have been explained by a diffraction effect that may be visualized by the formation of standing waves or electron backscattering within the molecule. This suggestion would explain the hump as well as the de Broglie analysis done in Ref. [8] without introduction of discrete peaks in the two-electron energy sharing or new DPI mechanisms. However, detailed theoretical analysis is crucially needed to fully resolve this problem.

To conclude, we have studied in a final state selective experiment the recently discovered phenomenon of a new DPI mechanism called Cooper pair formation using a magnetic-bottle time-of-flight two-electron coincidence setup. The experiment confirms the discovery of a hitherto unseen resonance in the DPI cross section of benzene and shows that such resonance is not present in pyrrole. The analysis of excess energy sharing profiles from coincidence data, however, contradicts the proposed reason for the new DPI mechanism. We have also shown that combining noncoincident ion and *e-e* coincidence yields recorded as a function photon energy can be used as a novel way to estimate the dication dissociation threshold of molecules.

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