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Photoemission of Cooper pairs from aromatic hydrocarbons

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We report the discovery of the formation of an electron Cooper pair approximately 40 eV above the double-ionization threshold in benzene, naphthalene, anthracene, and coronene after absorption of a single photon. We have measured the ratios of doubly-to-singly charged parent ions of the above mentioned molecules as well as pyrrole and furan using monochromatized synchrotron radiation up to 100 eV above the corresponding thresholds. We also recorded photoelectron spectra of benzene and naphthalene at selected energies. The electron-pair formation is based on the specific structure of the molecules and does not exist for pyrrole and furan.

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A photon of sufficient energy can interact with a single electron that is bound in an atom or molecule leading to photoemission of that electron leaving behind a singly charged ion. However, due to electron correlations the emission of two electrons by a single photon, called double photoionization, is also possible. Many investigations of the double-photoionization process using different techniques have been performed on atoms (see, e.g., [1, 2]) and small molecules (see, e.g., [3–6]) over several years. However, most of these investigations were limited to smaller molecules consisting of less than 6 atoms or were performed for larger molecules albeit at only a very few photon energies, so that the dynamics of the double-photoionization process in molecules remained unknown. A recent double-photoionization experiment on acenes [7] found that the ratio of doubly to singly charged parent ions increases with the length of the molecule and that the double-photoionization process is dominated by the same mechanism as for atoms for energies up to about 30 eV above threshold.

Here we continue to investigate the influence of the structure of a molecule on the double-photoionization process. In this Letter we report the discovery of the formation of a single quasiparticle state, which can be considered as a generalized Cooper pair, in benzene, naphthalene, anthracene, and coronene, and its subsequent emission from the molecule after photoabsorption. Aromatic hydrocarbons are discussed in the literature as candidates for high-temperature superconductors [8, 9] and our findings may help to better understand the mech-

anisms in organic superconductors such as metal-doped organic molecules [10] and graphene [11].

We have measured the ratios of doubly to singly charged molecular parent ions of benzene (C_6H_6 , Sigma-Aldrich, 99.9% purity), partially deuterated benzene ($C_6H_3D_3$, Sigma-Aldrich, 98% purity), naphthalene ($C_{10}H_8$, Alfa-Aesar, 99.6% purity), anthracene ($C_{14}H_{10}$, Alfa-Aesar, 99.9% purity), coronene ($C_{24}H_{12}$, Sigma-Aldrich, 97% purity), pyrrole (C_4H_5N , Sigma-Aldrich, 98% purity), and furan (C_4H_4O , Alfa-Aesar, 99% purity) at the 6m-TGM beamline [12] and the PGM undulator beamline [13] of the Synchrotron Radiation Center (SRC). The liquid samples were freeze-pump-thawed three times to remove gases from the vial holding the sample. The vial containing the powder naphthalene was pumped for about 30 minutes before use. The powders anthracene and coronene were heated in a crucible to 33 °C and 134 °C, respectively. For both the ion and electron experiments the chambers' base pressures were in the 10^{-9} mbar range. The sample gas pressure was about 1.0×10^{-6} mbar and 2.0×10^{-7} mbar for the ion and electron experiments, respectively.

An ion time-of-flight spectrometer [14] operated in the pulsed extraction mode separated the ions of different mass-to-charge ratios. The ions created in the field-free interaction region between pusher and extractor plate were pushed every 0.1 ms through the grounded extractor plate by applying a voltage pulse to the pusher plate. The ions then flew through a drift tube which has a Z-stack of microchannel plates at its end. Because of the long

pulse period only long-lived metastable or fully stable ions were detected. We used partially deuterated benzene in the ion experiment because the fragment $C_3H_3^+$ and the doubly charged parent ion, $C_6H_6^{2+}$ have the same mass-to-charge ratio whereas $C_6H_3^+D_3^{2+}$ does not have a corresponding fragment of the same mass-to-charge ratio. The photoelectrons were measured using a spherical sector-plate electrostatic analyzer mounted perpendicular to the photon beam direction on a turntable [15]. This setup allowed us to set the detector at the magic angle where the spectral intensities are independent of the angular distribution of the photoelectrons within the dipole approximation.

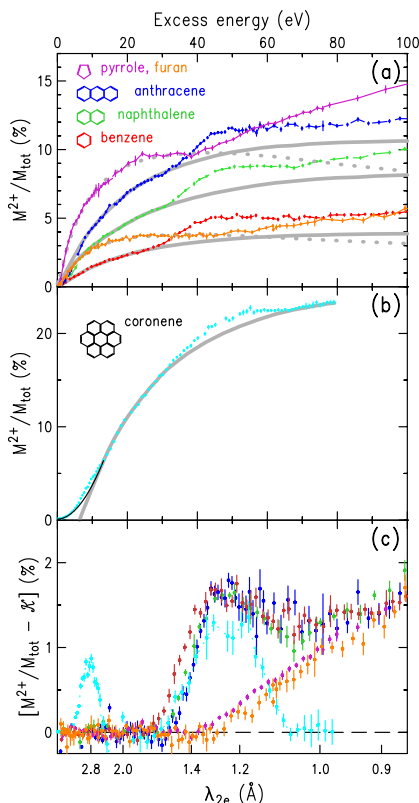


FIG. 1: (color online). (a) Measured ratios of doubly charged parent ions to all parent ions for partially deuterated benzene (red), naphthalene (green), anthracene (blue), pyrrole (purple) and furan (orange). The gray curves are scaled double-to-total photoionization ratios of He [16]. Note that the data for benzene, naphthalene, and anthracene below 30 eV have already been published [7]. (b) Same as (a) but for coronene (cyan). The solid black line is a fit curve to the low energy data. (c) Ratios, shown in (a) and (b), after subtracting the corresponding scaled He curves using the same color code. The data for pyrrole and furan are divided by 4 and 1.5, respectively, for easier comparison. The bottom axis shows the de Broglie wavelength of a two-electron pseudoparticle.

The measured double-to-single photoionization ratios R_s of the corresponding parent ions were converted to the ratio of doubly charged to all parent ions R_a using

$R_a = 1/(1/R_s+1)$ and is shown as a function of excess energy (photon energy minus double-ionization threshold) in Figs. 1(a) and 1(b) assuming that triple photoionization can be neglected. The solid gray curves are the He double-to-total photoionization ratios scaled in height to match the molecular ratios at energies below 30 eV [7]. The dotted gray curves are the He ratio scaled in height *and* energy to match the pyrrole and furan ratio data, respectively. The ratio R_a for coronene (Fig. 1(b)) shows a pronounced delayed onset. Thus we applied a (nearly) parabolic fit curve to the low energy data ($E < 6$ eV) and fitted the He curve to the coronene data in the 18–33 eV region. Both extrapolated fit curves merge smoothly at about 13 eV. We subtracted from the molecular ratios the corresponding gray curves, which describe the contribution of a double-photoionization mechanism called knock-out [7]. In the case of coronene the He curve was replaced by the “smooth” curve created from two fit curves described above.

It becomes evident in Fig. 1(c) that the humps in the ratios are of very similar magnitude and almost the same width for benzene, naphthalene, anthracene, and coronene *without* scaling the molecules’ ratios. This points to an effect independent of the electronic structure of the molecules. Interestingly, pyrrole and furan, five-membered aromatic rings, do not show the hump at all, but a simple linear increase of the ratio above about 42 eV emerges that seems to be present in the other molecules as well for the energy range under investigation except for coronene. The steady linear increase of the ratio above 42 eV may point to another double-photoionization mechanism, whose character is unknown to us and is still under investigation.

Previous investigations on C_{60} revealed a hump in the double-to-single photoionization ratio [17] when the corresponding de Broglie wavelength of an electron matched the distance between two carbon atoms. Such a match is achieved here only when we consider a particle of twice the electron mass. If the particle’s de Broglie wavelength equals the distance between two neighboring carbon atoms of about 1.4 Å [18], then its energy is about 38.3 eV, which coincides with the lower edge of the hump (Fig. 1(c)). While the bond lengths are not exactly the same for the different molecules (and not always exactly the same within a molecule), aromatic C-C bonds are about 1.4 Å which is consistent with our data.

The humps are “geometrical” resonances and, thus, the widths are not associated with a lifetime of an electronic state. The widths of the humps may be related to the size of the ring-shaped orbitals (above and below the ring of carbon atoms) created by the overlapping *p* orbitals.

In simultaneous double photoionization both electrons can share the available energy in any way possible including both having the same energy [19]. If the de Broglie wavelength of the electron pair matches the periodic structure of Coulomb potentials (as given by the

carbon atoms), then the two electrons can form a single pseudoparticle that is emitted from the molecule before breaking into two individual electrons. This highly correlated pair of electrons moves along a path equivalent to a one-dimensional lattice formed by the Coulomb potentials of the carbon atoms. This notion has already been put forward in Ref. [20] where an aromatic molecule is regarded as a ‘structure of positive carbon ions in a ring surrounded by a gas of free electrons.’ Even electron-pair formation has already been considered theoretically in a more general context for a one-dimensional chain of Coulomb potentials [21, 22].

Theoretical models have expected aromatic molecules to support ring currents due to the p orbitals that overlap above and below the ring of carbon atoms forming a delocalized π system [23]. The ring currents discussed in the literature [24–27] are calculated based on an external magnetic field, whereas in our experiment the resonant ring currents are created via photoionization.

At the right photon energy, benzene, naphthalene, anthracene, and coronene seem to allow the formation of a 2-electron pseudoparticle, dubbed Cooper pair, whose de Broglie wave is a closed loop in the system of overlapping π bonds. Pyrrole and furan, on the other hand, are both five-membered rings having a different shape and geometrical symmetry than benzene and, thus, do not show the hump at all. While all molecules showing the hump do have a point symmetry regarding their carbon atoms, pyrrole and furan do not have one.

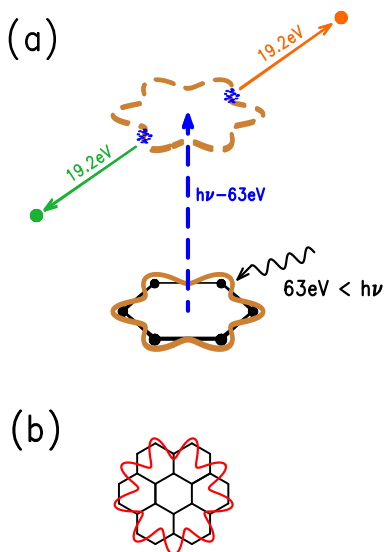


FIG. 2: (color online). (a) Schematic diagram for the formation and photoemission of a Cooper pair. The dark grey (brown) line represents the de Broglie wave along the benzene molecule, whose wavelength matches the C-C distance. When the pair leaves the molecule it breaks up emitting the two electrons initially back-to-back in the electron-pair frame (arrows). (b) A closed-loop de Broglie wave with a wavelength of twice the C-C distance around coronene.

After a Cooper pair has been created, the additional energy of the photon will be used to emit that pair from the molecule. As the Cooper pair is emitted, the associating influence of the periodic structure of Coulomb potentials on the electron pair diminishes, the closed-loop de Broglie wave can no longer be maintained, and the pair breaks up into individual electrons as visualized in Fig. 2(a).

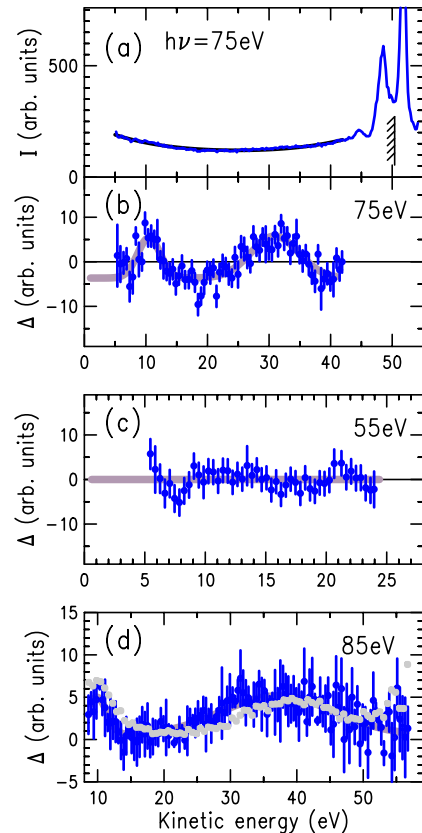


FIG. 3: (color online). (a) Photoelectron spectrum of benzene taken at 75 eV photon energy [grey (blue) line]. The black line is a fit curve to the double-ionization continuum in the spectrum. The double-ionization threshold is indicated. (b) Difference Δ between the measured spectrum and the fit curve (circles with error bars) shown in (a). The grey line is an asymmetric Voigt fit curve to the data. (c) same as panel (b) but for 55 eV. (d) same as panel (b) but for naphthalene (dark grey/blue) and benzene (grey circles), both taken at 85 eV photon energy. The benzene data are scaled in intensity for better comparison and their error bars were omitted here for clarity.

Ring currents in polycyclic aromatic hydrocarbons can have various paths within these molecules [26–28]. Coronene, in contrast to the other molecules discussed here, is large enough to easily accommodate a wave along its outer rim that has a wavelength of twice the C-C distance (Fig. 2(b)). Indeed, Fig. 1(c) shows a prominent hump around 10 eV corresponding to a wavelength of 2.8 Å confirming the existence of a de Broglie wave of twice

the C-C distance ($2 \times 1.4 \text{ \AA}$).

To corroborate the notion of the emission of a Cooper pair, we measured photoelectron spectra of benzene and naphthalene. It is known from He photoelectron spectra that the energy distribution of two simultaneously emitted electrons is U-shaped [19], becoming flat near threshold. The benzene photoelectron spectrum taken at 75 eV photon energy exhibits, at a first glance, the expected U-shaped continuum that can approximately be modeled by a fourth-order polynomial (Fig. 3(a)). However, after subtracting the fit curve from the spectrum, two broad peaks become visible (Fig. 3(b)) showing that it was not an ideal fit curve. On the other hand, a fourth-order polynomial fit to a similar looking He spectrum does not result in any remaining features. We conclude that the fit curve is adequate for modeling the continuum but leaves any structure on top of that continuum intact.

These broad peaks appeared in other benzene spectra taken at different photon energies but not at 55 eV, which is below the onset of the hump (Fig. 3(c)). A naphthalene photoelectron spectrum taken at 85 eV exhibits almost the same two-peak structure that we see in benzene (Fig. 3(d)).

The energy positions of both electron peaks exhibit a smooth change with excess energy (Fig. 4). Note that although both electrons have initially the same magnitude of momentum in the electron-pair frame, the addition of the Cooper pair's momentum yields different energies in the lab frame. If the breakup of both electrons was isotropic, their final kinetic energies in the lab frame would lie between the solid lines shown in Fig. 4. However, the breakup of the Cooper pair may happen soon after it has left the molecule, and the remaining doubly charged parent ion may influence the breakup process and the emission angles.

The dashed line corresponds to the symmetric case where both electrons break up perpendicular to the momentum of the Cooper pair. Our data indicate that the most probable case (maximum of the broad electron peaks) is a breakup of the pair at angles of 70° and 138° relative to the Cooper pair momentum (0°) in the lab frame for the faster and slower electron, respectively. The fact that we do not see a back-to-back emission can be explained by the presence of the residual doubly charged ion. When the pair breaks up in the vicinity of the doubly charged ion both electrons have enough energy to escape but the molecular Coulomb potential alters their direction with the slower electron pulled back more than the faster one. This process is similar to the post-collision interaction effect involving all three bodies (two electrons and one ion).

The dotted lines were calculated using these angles in the pair frame. Note that the rather large widths of the peaks in the photoelectron spectra mean that a wide range of angles around those values are possible. The agreement between the calculated curves and data is sat-

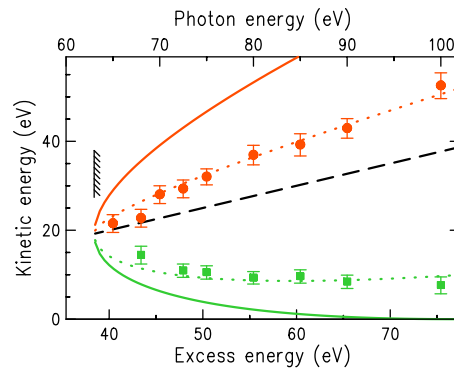


FIG. 4: (color online). Both photoelectron peak positions (dark grey/orange circles and light grey/green squares) as a function of photon energy (top axis) and excess energy (bottom axis). The solid lines correspond to emission angles of 0° and 180° with respect to the emission direction of the Cooper pair (0°). The dashed line corresponds to a breakup of the two electrons perpendicular to the emission direction of the pair. The dotted lines correspond to emission angles of 70° and 138° . The angles are given in the frame of the electron pair. The threshold for Cooper pair emission is indicated.

isfactory overall. However, at low photon energies the doubly charged parent ion may have more influence on the breakup process and the most probable emission angles will change.

While our data suggest the formation and emission of 2-electron pseudoparticles, dubbed Cooper pairs, in some aromatic hydrocarbons, there is, as of now, no connection to superconductivity as there is no *long-range* electron correlation. On the other hand, aromatic hydrocarbons are prime candidates for organic superconductors and our findings may help to understand the mechanism for superconductivity in high-temperature superconductors.

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