PHYSICAL REVIEW A **91**, 063419 (2015)

Role of the nitrogen atom in double photoionization of monocyclic hydrocarbons

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(Received 26 March 2015; published 25 June 2015)

We report about possible formation of highly correlated electron pairs in the heterocyclic aromatic hydrocarbons pyridine, pyrimidine, and 1,3,5-triazine. Previously, these electron pairs have been observed in the acenes and in coronene, but not in pyrrole and furan. Our measurements presented here shed some light on the conditions for electron-pair formation and emission. Aromatic hydrocarbons are discussed as candidates for high-temperature superconductors and our findings may help to better understand the mechanisms in organic superconductors.

DOI: 10.1103/PhysRevA.91.063419 PACS number(s): 33.80.Eh

I. INTRODUCTION

In a previous study it was discovered that electron-pair formation following photoabsorption is possible for the acenes (e.g., benzene) and coronene [1,2]. However, no evidence for electron-pair formation in the heterocyclic hydrocarbons pyrrole, furan [1], selenophene [3], and thiophene [4] has been observed. Here, we want to shed more light on the mechanism for the formation of these two-electron pseudoparticles by presenting results for the aromatic molecules pyridine, pyrimidine, and 1,3,5-triazine, which are benzene rings with one, two, and three carbon atoms replaced by nitrogen atoms. We note that the previously suggested model of electron-pair formation is only one possible interpretation that describes the observed experimental data, but other interpretations may also be possible. However, there are no other interpretations published at this time. The molecules investigated here are of biophysical importance since they represent the main structure of the nucleobases cytosin, thymine, and uracil, and the migration of electrons inside biological molecules is of current interest. In addition, aromatic hydrocarbons are prime candidates for organic superconductors [5,6] and our findings may help to understand the mechanism for superconductivity in high-temperature superconductors such as metal-doped organic molecules [7] and graphene [8].

Previously it was concluded that pyrrole, furan, selenophene, and thiophene do not support the formation of two-electron pseudoparticles "because these are five-membered rings having a different shape and geometrical symmetry than benzene" [1]. While a recent paper [9] confirms our observation of a possible resonant pairing mechanism, it also claims that the absence of this mechanism is possibly due to the nitrogen atom in pyrrole, which would point to the importance of the electronic structure rather than the geometrical structure of the molecule.

The formation of two-electron pseudoparticles can be investigated via the double-photoionization process in which the absorption of a single photon results in the emission of two electrons simultaneously from the molecule. This fundamental process is due to electron correlations and has been studied extensively on atoms (see, e.g., Refs. [10,11]) but also on molecules (see, e.g., Refs. [12–14]). A particular interesting group of molecules are aromatic hydrocarbons because of the overlapping p_z orbitals that form a π orbital consisting of two rings above and below the molecules' plane in which electrons can move freely, and ring currents can be created by, for example, applying an external magnetic field.

II. EXPERIMENT

We have measured the ratios of doubly to singly charged molecular parent ions of pyridine (C_5H_5N, Sigma-Aldrich, 99.8% purity), pyrimidine ($C_4H_4N_2$, Alfa-Aesar, 99% purity), and 1,3,5-triazine ($C_3H_3N_3$, Alfa-Aesar, 97% purity) over a wide range of incident photon energies at the 6-m toroidal-grating monochromator (6m-TGM) beamline [15] 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 sticky powder 1,3,5-triazine was pumped on for about 30 min before starting the experiment. The base pressures of the sample chamber were in the 10^{-9} mbar range. The sample gas pressure was about 1.0×10^{-6} mbar during the experiment.

An ion time-of-flight spectrometer [16] operating in the pulsed-extraction mode separated the ions of different mass-to-charge ratios. The pulse period was 0.1 ms so that only long-lived metastable or fully stable ions were detected.

In order to analyze the double-photoionization process for the molecules mentioned above, we divided the ion yield of doubly charged parent ions by the yield of singly charged parent ions. In the following text the term *ratio* refers to the ratio of doubly to singly charged parent ions.

III. RESULTS AND DISCUSSION

The results for pyridine (a ring with *one* nitrogen atom in it) are presented in Fig. 1. Using the same analysis procedure as before [17] we fitted the curve of the helium double-to-single photoionization ratio [18] to our pyridine ratios for excess energies below 28 eV [solid red (gray) line in Fig. 1(a)]. In the energy range discussed here the scaled He ratio curve represents the contribution from the so-called knock-out mechanism [19,20]. Unfortunately, the peak of the doubly charged parent ion in the spectrum is rather weak and very close to a prominent fragment peak ($C_3H_3^+$ and C_2HN^+) so that even a least-squares fit did not yield reliable results for the area of the doubly charged ion at energies close to the double-ionization threshold. Therefore, the ratio values do not go down to the threshold, and, thus, we can only estimate the

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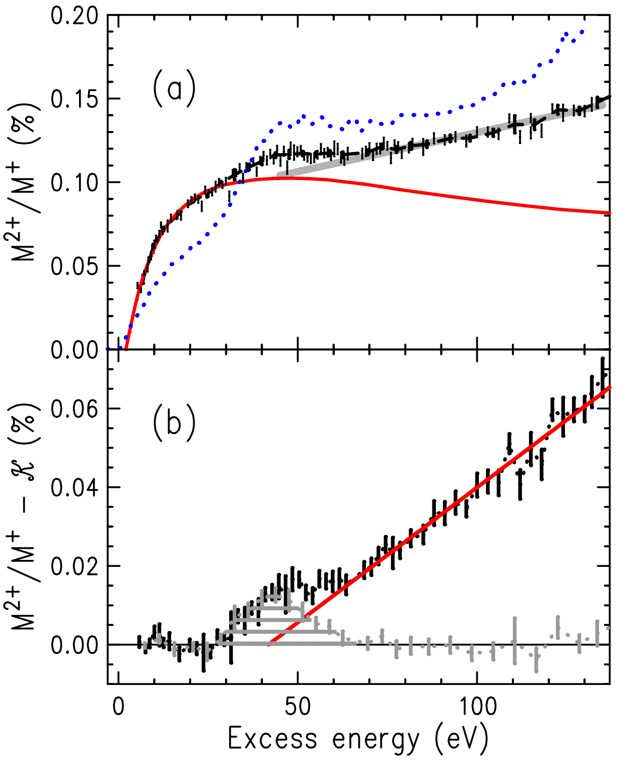

FIG. 1. (Color online) Results for pyridine: (a) Measured ratios of doubly to singly charged parent ions (black data) compared to the scaled ratio for partially deuterated benzene [1] (blue [gray] dotted line). The thin solid (red [gray]) line is a fit of the He ratio curve [18] to the pyridine data at energies below 30 eV. The thick gray line describes the high-energy behavior of the ratio. (b) The measured ratio after subtracting the fit curve shown in panel (a) (black data) and after additionally subtracting the straight fit curve (red [gray]solid line) in panel (b) (gray data). The shaded area indicates an increased double-photoionization yield due to the formation of two-electron pseudoparticles.

double-ionization threshold, which is approximately 18.0 eV. The excess-energy scale in Fig. 1 was obtained by subtracting this threshold energy from the photon energy. We note that the conclusions drawn in this paper do not require an exact value of this threshold. Figure 1 shows a greatly reduced ratio compared to benzene [1]. The benzene ratio curve in Fig. 1(a) (dotted blue [gray] line) is scaled so that the maxima of the knock-out contributions for both molecules are of equal height.

After subtracting this fit curve from our pyridine ratios we obtain the black data shown in Fig. 1(b). Those reduced ratios are, of course, near zero for energies below 28 eV. At energies above 70 eV we find experimental evidence for a straight linear increase of the ratio [solid red (gray) line in Fig. 1(b)]. The origin of this linear increase is still unknown. We extrapolated this linear fit curve down to zero and subtracted it from reduced ratios in Fig. 1(b), resulting in the gray data points. Note that the scatter of the data points around the linear fit curve is due to statistical uncertainty. With this procedure we obtain a hump indicated as a shaded area in Fig. 1(b). This hump has been observed before in benzene and other molecules with a hexagonal structures and has been recently confirmed for benzene [9].

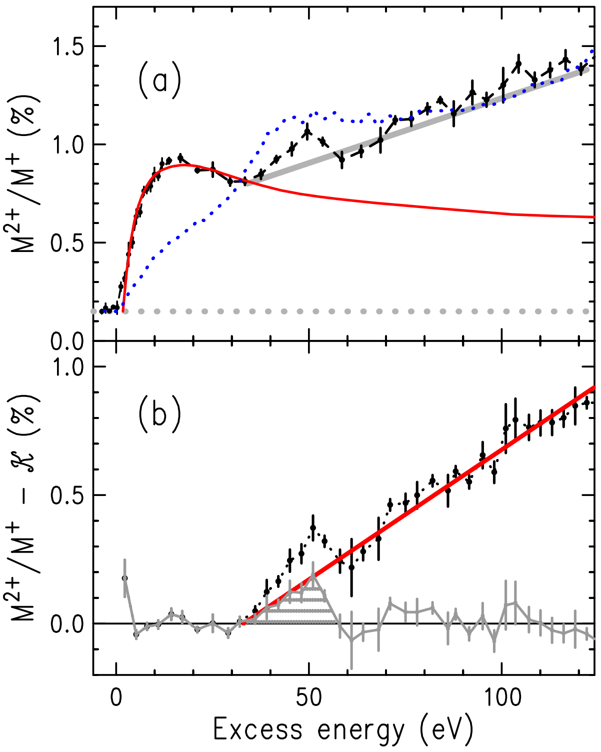

FIG. 2. (Color online) Same as Fig. 1 but for pyrimidine.

Briefly, this hump is possibly due to the formation of two-electron pseudoparticles, which have a de Broglie wavelength that approximately matches the bond lengths in the ring, so that the wave forms a closed loop. For a more detailed discussion, see Ref. [1]. It is reasonable to assume that the electron pair is not exactly above (or below) the ring of atoms but is in the π orbital that has a slightly larger diameter due to the hydrogen atoms attached to the carbon atoms in the ring. At this point we can already conclude, in variance with a recent report [9], that the nitrogen atom in pyrrole is not the reason for the absence of the hump because pyridine contains a nitrogen atom.

Naturally, the question arises of whether a second nitrogen atom would reduce the ratio further. Figure 2 shows our results for pyrimidine, which is a benzene ring with *two* carbon atoms replaced by nitrogen atoms that have one carbon atom between them. In contrast to pyridine, we were able to determine an accurate double-ionization threshold, which is 20.94(17) eV. As one can see, the ratio for pyrimidine is generally higher than for pyridine. We applied the same procedure to analyze the ratio of pyrimidine and obtain again a hump that is indicated by the shaded area in Fig. 2(b).

In Fig. 3 we present the ratios for 1,3,5-triazine, which is a hexagonal ring with alternating carbon and nitrogen atoms. We determined the double-ionization threshold to be at 25.7(18) eV. As in the case of the two molecules discussed above, we obtain a hump demonstrating the formation of a two-electron pseudoparticle. We have included in Fig. 3(b) the hump for benzene scaled in height (solid blue [gray] line) according to the maxima of the knock-out contributions for these molecules. We can readily see the similarity in the shape of the humps but, more importantly, we also see clearly an energy shift of the 1,3,5-triazoine hump with respect to the benzene

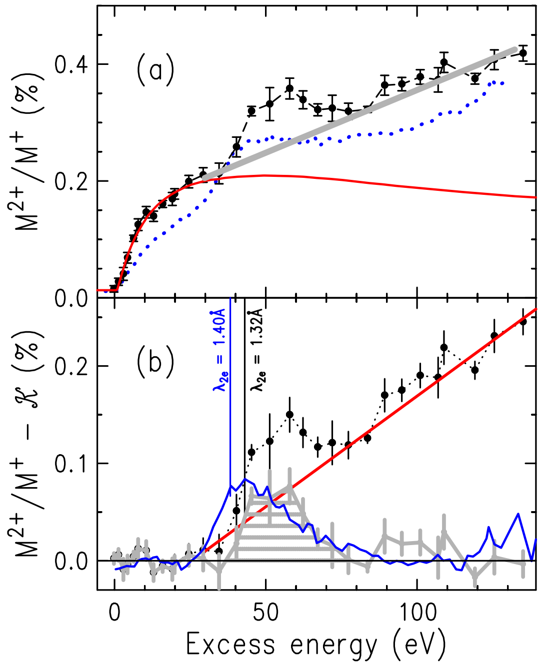

FIG. 3. (Color online) Same as Fig. 1 but for 1,3,5-triazine. In addition, panel (b) shows the corresponding hump for benzene (solid blue [gray] line) scaled in height. The energy shift due to the different bond lengths in 1,3,5-triazine and benzene is indicated.

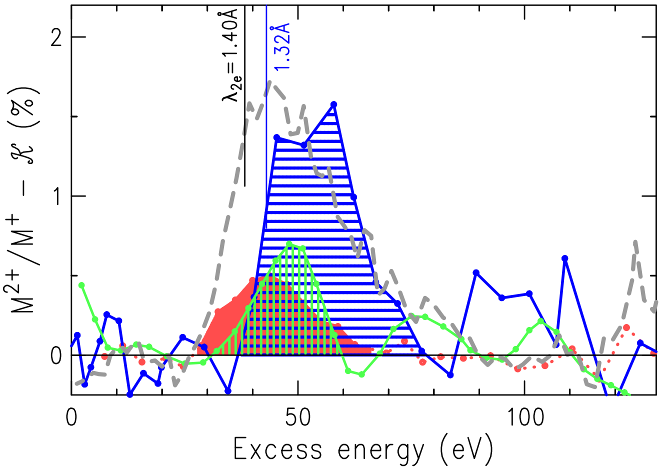

FIG. 4. (Color online) The humps in the ratios of doubly to singly charged parent ions shown as a gray-shaded area in the figures above (pyridine: filled [red] area; pyrimidine: vertical [green] lines; 1,3,5-triazine: horizontal [blue] lines) together with the hump for benzene (dashed gray line).

hump. This energy shift can be explained by the reduced length of C-N bonds compared to C-C bonds. This is a clear indication that the bond length affects directly the position of the hump. The C-C bond length is 1.399(1) Å [21], whereas the C-N bond length is reported as 1.319 Å based on x-ray diffraction [22]. The corresponding energies for the de Broglie wavelengths of 1.4 and 1.32 Å of a two-electron pseudoparticle are indicated in Fig. 3(b). This energy shift, based on the different bond lengths, is indeed approximately the same energy shift as for the humps in benzene and 1,3,5-triazine.

Figure 4 summarizes our results by comparing the humps, which were shown as shaded areas in Figs. 1(b)–3(b), scaled in height according to their knock-out contributions to their ratios with respect to benzene. The (not scaled) benzene hump is the largest hump followed by the almost as tall 1,3,5-triazine hump. Pyrimidine and pyridine exhibit smaller humps. In other words, based on the ratios normalized to the respective maxima of the knock-out contributions, we obtain a systematic change in height of the hump. As more nitrogen atoms are in the ring, the hump becomes taller, except for benzene. This can be explained by the geometrical symmetry of the molecules. While pyridine with only one nitrogen atom has low symmetry, 1,3,5-triazine with its alternating carbon and nitrogen atoms has a high symmetry (and a constant bond length in the ring), a property that may be important if vibrations of the atoms in the ring are a factor in the possible formation of two-electron pseudoparticles. However, right now the mechanism for the formation of electron pairs is not known. In Ref. [1] it was suggested that this two-electron pseudoparticle can be regarded as a Cooper pair that moves in the π orbital and is experiencing a one-dimensional lattice formed by the Coulomb potentials of the atoms in the ring. The idea of an aromatic molecule that is viewed as a "structure of positive carbon ions in a ring surrounded by a gas of free electrons" [23] is not new, and even electron-pair formation has already been considered theoretically in a more general context for a one-dimensional chain of Coulomb potentials [24,25]. A very recent publication about Cooper pairs in aromatic molecules [26] suggests that the "ring structure is crucial as the circular structure forces several energetically favorable conditions which might be otherwise competing in a linear model."

However, we also want to mention a different mechanism, namely the formation of *Coulomb* pairs introduced in Ref. [27], noting that "perhaps the simplest physical manifestation of the phenomenon under discussion (Coulomb pairing) is provided by the delocalized motions of paired electrons in a benzene ring structure." This pairing mechanism is discussed further in Ref. [28].

The influence of the bond lengths in the molecules is also highlighted in Fig. 4. As discussed above, the 1,3,5-triazine hump exhibits the largest energy shift, while pyrimidine has a smaller shift, and pyridine has no noticeable shift. The average bond lengths for each of the molecules pyridine, pyrimidine, and 1,3,5-triazine are 1.375, 1.358, and 1.319 Å [22], respectively, and changes in accord with our observation summarized in Fig. 4.

IV. CONCLUSIONS

In conclusion, we have demonstrated that the nitrogen atom in pyrrole is not the reason for the lack of electron-pair formation, as suggested in a recent report [9]. We note that this paper does confirm a resonant mechanism in benzene.

Three different molecules, pyridine, pyrimidine, and 1,3,5-triazine, that contain one, two, and three nitrogen atoms, respectively, do show a clear hump in their ratios of doubly to singly charged parent ions indicative for electron-pair formation. The most symmetric molecule in this investigation, 1,3,5-triazine, exhibits a rather strong hump compared to its overall small ratio. Note that the bond lengths in the triazine ring are also all the same, in contrast to the other two molecules investigated here.

Second, we did find an energy shift of the hump in accordance with the average bond lengths in the individual molecules. As the average bond length changes, the de Broglie wavelength has to changes accordingly to be resonant with the distances, resulting in an energy shift of the resonance energy where the hump is observed.

ACKNOWLEDGMENTS

The authors are grateful for assistance by the SRC staff. We also thank Prof. Dave Huber for many stimulating discussions and Dr. Pavle Juranić for a critical reading of the manuscript. This work is based upon research conducted at the SRC, University of Wisconsin–Madison, which was mainly supported by UW Graduate School and SRC Users.

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