Origin of the low energy resonance in the double photoionization of pyrene and coronene, and its absence in the double photoionization of corannulene

Ralf Wehlitz\textsuperscript{*} and David L. Huber\textsuperscript{†}

Physics Department, University of Wisconsin–Madison, Madison, Wisconsin 53706, USA

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Abstract

The low energy resonance in the double photoionization of the aromatic hydrocarbons pyrene ($C_{16}H_{10}$) and coronene ($C_{24}H_{12}$) is investigated theoretically using an approach based on the one-dimension Hubbard model for $\pi$-conjugated systems with nearest-neighbor interactions. The Independent Subsystem Approximation, where the perimeter and interior carbon atoms are treated as independent entities, is employed. Since no low energy resonances have been found in aromatic hydrocarbons where there are only perimeter carbon atoms, we attribute the low energy resonances in pyrene and coronene to the interior carbon atoms. However, corannulene ($C_{20}H_{10}$) having five interior carbon atoms does not exhibit a low-energy resonance in the experimental data. We attribute the absence of this resonance to the odd number of interior carbon atoms.

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\textsuperscript{*}rwehlitz@gmail.com

\textsuperscript{†}dhuber@wisc.edu
I. INTRODUCTION

The double-photoionization (DPI) process, i.e., the removal of two electrons by a single photon, has been investigated for various aromatic molecules using synchrotron radiation in recent years. A convenient quantity to study the DPI process in atoms and molecules is the ratio of doubly to singly charged ions as a function of photon energy.\[1\] Common to all atoms and molecules is the knock-out mechanism\[2\] in which the photoionized electron knocks out a second electron, leading to a helium-like ratio curve. In the case of molecules, it has been discovered that additional photoionization mechanisms, not observed for atoms, can contribute to the production of doubly charged molecular ions.\[3\]

For aromatic molecules with 5-member rings (pyrole, furan, selenophene)\[4\] and for the aromatic molecule with the 7-member ring (tropone)\[5\] the ratio curves show a linear increase in the ratio above a certain threshold, which is far above the double-ionization threshold. It has been proposed that the linear increase is associated with the simultaneous emission of two electrons with equal kinetic energy and opposite momenta.\[6, 7\]

In the case of the aromatic molecules with 6-member rings (e.g. pyrrole, benzene, halogenated benzene, pentacene, pyridine, triphenylene, coronene) an additional broad peak in the ratio is present. For these molecules, the broad peak is essentially at the same value of the energy and is only slightly changed by introducing nitrogen atoms into the ring (pyridine, pyrimidine, 1,3,5-triazine)\[8\] or by replacing hydrogen atoms with halogen atoms ($C_6\text{BrF}_5$).\[9\]

There are two explanations for the origin of this peak. In the first, the peak is associated with the break-up of a Coulomb-pair whose formation was studied by Mahajan and Thyagaraga.\[10\] In the second explanation, the peak is associated with the formation of a “Cooper pair” whose de Broglie wavelength approximately matches the carbon–carbon distance of the molecule leading to a standing wave in the $\pi$ orbital.\[11\] It is worthwhile to mention that the $\pi$ orbital is essential for this feature. An experiment on tribromoborazine $[(\text{BrBNH})_3]$, a molecule with a 6-member ring of boron and nitrogen atoms, does not show any peak in its ratio curve but only the contribution of the knock-out mechanism and a linear increase of the ratio.\[12\]

Recently it has been shown that the DPI curves of chlorobenzene and fluorobenzene have a resonance at the onset of the molecular DPI near 4 eV.\[13\] This resonance has been
interpreted in their paper as being due to the de Broglie wavelength of the two-electron pair matching the size of the conjugated $p-\pi$ orbital.

![Graph showing DPI ratio as a function of photon energy with different shaded areas representing contributions from knock-out mechanism and the ratio after subtraction.]  

**FIG. 1.** Extended plot of the DPI ratio $R = M^{2+}/(M^{1+} + M^{2+})$ of pyrene as a function of photon energy (open circles). $M^{1+}$ and $M^{2+}$ are the yields of singly and doubly charged parent ions, respectively. The dark (green) shaded area represents the contribution from the knock-out mechanism. The red (filled) circles represent the ratio after subtracting the knock-out contribution, which rises linearly above 95 eV.

Two of the molecules investigated here (pyrene and coronene) exhibit peaks in their ratios about 10 eV above the DPI threshold. These peaks are distinct from the resonances studied in Ref. [13] which we did not observe in our studies probably due to the larger energy-step size. Figure 1 illustrates the effect of the different mechanisms contributing to the production of doubly charged parent ions of pyrene. In contrast to the molecules mentioned previously, pyrene and coronene have interior carbon atoms, i.e., atoms that are not located on the outer edge as shown in Fig. 2. In this paper, we will discuss a possible connection between the 10-eV peak and the interior carbon atoms. Section II describes the theoretical model used in our analysis, Section III and Section IV applies our model to pyrene and coronene, respectively. We discuss the absence of a 10-eV peak for corannulene in Section V. Our interpretation is summarized in Section VI.
II. THEORETICAL ANALYSIS OF LOW-ENERGY PEAK

The experimental results presented here are plots of the DPI ratio $R$ versus excess energy relative to the DPI threshold. $R$ is defined by the equation

$$R = \frac{M^{2+}}{M_{tot}} - K$$  \hspace{1cm} (1)$$

in which $M^{2+}$ and $M_{tot}$ denote the yields of doubly charged and singly plus doubly charged parent ions, respectively. The contribution from triply charged ions is assumed to be small and is not included in $M_{tot}$. $K$ denotes the knock-out contribution to the DPI process modeled by a scaled helium ratio curve.

In analyzing the low energy peaks near 10 eV, we make use of the Independent Subsystem Approximation, in which the perimeter and interior carbon atoms are treated as separate systems.\cite{6,15} The low energy resonance in pyrene is attributed to the interaction between the two $\pi$ electrons associated with the two interior carbon atoms. To understand this point, we focus our analysis on the 2-site Hubbard model. In one dimension, the Hubbard
model is equivalent to the Pariser-Parr-Pople model of $\pi$-conjugated systems where the 2-site Hamiltonian has the form\cite{16}

\begin{equation}
H = -t(c_1^c c_2 + c_1 c_2^c) + U
\end{equation}

in which $t$ denotes the electron transfer integral, $U$ is the interaction between two electrons occupying the same site and $c$ and $c^*$ denote electron annihilation and creation operators, respectively.

### III. PYRENE

An analysis of the photoexcited states in dimerized Mott insulators has been outlined by N. Maeshima and K. Yonemitsu.\cite{17} Equation (20) and related text in Section Vc of Ref.\cite{17} are directly applicable to the 2-site Hubbard model. The excitation energy of the model associated with the optical absorption, $E_0$, is expressed as

\begin{equation}
E_0 = U/2 + (U^2/4 + 4t^2)^{1/2}.
\end{equation}

Note that there is only a single excitation energy for the two-electron system. In our analysis of the DPI in pyrene, we identify the energy of the resonance peak relative to threshold with $E_0$. To obtain a theoretical estimate of $E_0$, we need values of both $U$ and $t$. Values for $U$ and $t$ reported in the benzene literature are 10.06 eV and 2.54 eV, respectively.\cite{16} The parameter $U$ is associated with a single carbon atom. As such, it is expected to be nearly the same for all carbon atoms in an aromatic molecule. In contrast, the parameter $t$ is associated with a pair of carbon atoms and will depend on the details of the electron transfer between the two, which can vary with the location of the pair.

The resonance in the DPI of pyrene is attributed to the absorption of a photon by the electron pair inside the perimeter of the molecule at the interior carbon atoms (cf. Fig. 2). This process promotes the molecule to an excited state. The molecule subsequently ionizes creating a pair of free electrons with total kinetic energy $E_0$. The experimental energy of the resonance $E_0$ in the DPI of pyrene shown in Fig. 3 is equal to $(10.5 \pm 1.0)$ eV.

An extension of the analysis, which is analogous to an approach followed in Ref.\cite{7} is to keep $U$ fixed at the benzene value, 10.06 eV. The value of $t$ is then adjusted to give the experimental energy of the peak, 10.5 eV. As shown in Fig. 4 the resulting value of $t$ is 1.07
FIG. 3. DPI ratio $R$ vs. excess energy relative to the DPI threshold for pyrene.\cite{14} $R$ is defined in Eq. (1).

FIG. 4. Excitation energy $E_0$ as a function of the transfer integral $t$ for a fixed value $U = 10.06$ eV using Eq. (3). The dotted line starting at $E_0=10.5$ eV corresponds to a $t$ of 1.07 eV, indicating that the value of the transfer integral of the two interior carbon atoms in pyrene is approximately $1/3$ of the benzene value of 2.54 eV.

IV. CORONENE

In coronene, there are six interior carbon atoms arranged in a benzene-like ring (cf. Fig. 2). In the Independent Subsystem Approximation, the interior atoms are treated as a separate system. In pyrene as well as coronene, each interior carbon atom has three nearest neighbors. The two molecules differ in that the interior carbon atom in pyrene has one
nearest-neighbor that is also an interior atom, whereas in coronene, the interior atoms have two interior nearest-neighbors. Therefore, the 2-site Hubbard model used for pyrene can, unfortunately, not be applied to coronene.

The experimental DPI data in Fig. 5 are evidence of a well-defined resonance at (9.4 ± 1.0) eV. The similarity of the profile of the 9.4-eV resonance in coronene to the profile of the 45-eV resonance in coronene and benzene suggests a common origin: the break-up of a closed-loop de Broglie wave of a two-electron pair. We note that we attribute the fluctuations in the ratio around 20 eV to experimental uncertainties.

V. CORANNULENE

In a recent publication,[18] the double photoionization ratio of corannulene was compared to the DPI ratio of coronene. It was found that while both molecules had a peak in the ratio near 50 eV, corannulene did not have the low energy peak that is discussed in Section IV. Since corannulene has a ring of five interior carbon atoms, the question arises as to why it has no peak, whereas coronene, with a ring of six interior atoms, has a peak at 10 eV. In a recent analysis of the high-energy corannulene data we have found linear behavior in the DPI ratio for photon energies above 150 eV, as displayed in Fig. 6. In this section, we will show that the 5-carbon array in corannulene cannot form a closed loop. Instead, there is an open array of carbon atoms that is the origin of the linear behavior in the DPI ratio.

The explanation for the difference in the DPI ratio between corannulene and coronene is
FIG. 6. High energy region of the DPI ratio of corannulene as defined in Eq. (1) after subtracting the contribution of the knock-out mechanism. The dashed line is to guide the eye.

FIG. 7. Interior carbon atoms of corannulene with the spins of their \( \pi \) electrons.

related to the orientation of the spins of the interior \( \pi \) electrons in their ground state which can be either “up” or “down”. In the coronene interior ground state, the six spins alternate between up and down and the total \( \pi \) spin moment is zero. In the corannulene case, where there are five interior \( \pi \) electrons, the interior ground state is more complicated since there cannot be a complete cancellation of the moments. In Fig. 7, we show an arrangement that minimizes the total moment of the 5-spin interior array.

The critical region in Fig. 7 is at the base of the pentagon, where the two down-spin \( \pi \) electrons are nearest neighbors. Because of the Exclusion Principle, it is impossible for a down-spin \( \pi \) electron on one of the base sites to transfer to the other base site. The effect of the Exclusion Principle is to introduce a 2-site “impurity” that eliminates the 5-site closed loop for \( \pi \) electrons that have down spins.
DPI in corannulene involves the two carbon atoms for which the $\pi$ electrons have up-spins and the carbon atom on the top of the pentagon where there is a $\pi$ electron with a down-spin. The emission involves one of the up-spin electrons and the down-spin electron. In Ref. [7] it is shown that when the DPI ratio is a linear function of the photon energy, the two electrons are emitted simultaneously with equal kinetic energy and opposite momenta.

As a final comment, we note the similarity in the asymptotic behavior of the DPI ratios of pyrene and corannulene. In both cases, linear behavior was observed above 100 eV. We attribute the similarity to the arrangement of the interior carbon atoms. In the case of pyrene, there is a single carbon pair, whereas in corannulene, there are two interior pairing configurations that contribute to the DPI ratio.

VI. SUMMARY

We have theoretically analyzed the resonance near 10 eV in the experimental DPI ratio of pyrene and coronene. Both molecules have interior as well as perimeter carbon atoms. Employing the Independent Subsystem Approximation, we can interpret the 10-eV resonance as being due to the interior carbon atoms. We also have presented an explanation for the absence of the 10-eV peak in corannulene.

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