Independent-subsystem interpretation of the double photoionization of pyrene and coronene

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Abstract

It is shown that the M$^{2+}$ ion yield in the double photoionization of the aromatic hydrocarbons, pyrene and coronene, can be expressed as a superposition of a contribution from a resonance involving carbon atoms on the perimeter and coherent contributions from carbon atoms inside the perimeter. In the case of pyrene, the two interior atoms are associated with a resonance peak at 10 eV and linear behavior above 75 eV. The resonance peak is an optically excited state of the interior carbon pair. The linear behavior arises from the coherent emission of two electrons with equal energy and opposite momenta, as occurs in pyrrole. Coronene has a low energy peak along with two pairing resonances, however, the linear region as in the case of pyrene is absent. The low energy resonance is associated with the atoms on the perimeter and the high energy resonance is associated with the hexagonal array of six carbon atoms at the center of the molecule. It is proposed that the quasi-independence of the contributions from the perimeter and interior atoms is related to Hückel’s Rule for the stability of aromatic hydrocarbons.

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I. INTRODUCTION

The photon-energy dependence of the simultaneous removal of two electrons from an atom or molecule by a single photon has been studied for several cases (see, e.g., [1]). In recent publications [2, 3] the double photoionization (DPI) results for the aromatic hydrocarbons pyrene and coronene using monochromatized synchrotron radiation over a wide range of energies have been reported. The general goal of these investigations is to elucidate the role of the physical molecular structure on the DPI process. A unique feature among the hydrocarbons studied using DPI is that pyrene and coronene have carbon atoms located inside their molecular perimeter as well as on their perimeter [4]. The chemical formula of pyrene is C_{16}H_{10} with 14 carbon atoms on the perimeter and two carbon atoms in the interior, positioned as nearest-neighbors. Coronene has the formula C_{24}H_{12} with 18 carbon atoms on the perimeter and six carbon atoms in the interior that are arranged in a benzene-like ring. The focus in this paper is the role played by carbon atoms inside the perimeters of the two molecules on DPI. We will discuss that the perimeter carbon atoms and the interior carbon atoms can be regarded as independent subsystems in the DPI process. The current analysis of the experimental data was undertaken in light of the previous theoretical studies of DPI in aromatic hydrocarbons [5, 6].

Our results are presented in plots of the DPI ratio vs excess energy relative to the DPI threshold. Here, the DPI ratio is defined by the expression

\[ R = \frac{M^{2+}}{M_{\text{tot}}} - K, \]  

where \( M^{2+} \) and \( M_{\text{tot}} \) denote the yields of doubly charged and singly plus doubly charged parent ions, respectively. \( K \) is the knock-out contribution [4] to the DPI process, in which the first electron on its way out of the molecules knocks out a second electron. The contribution from the knock-out mechanism is modelled by the double-to-total photoionization ratio of helium, which is justified for photon energies as low as in this study. We begin our analysis with pyrene and coronene, and will then test our model of independent subsystems on anthracene.
II. PYRENE

In pyrene, after subtracting the contribution from the knock-out mechanism to the DPI ratio as discussed in [3], there are three regions in the photon energy spectrum with distinctly different behaviors in the DPI: (i) a low-energy region, with a comparatively sharp resonance peak at 10 eV above the DPI threshold, (ii) a mid-range region with a 25 eV onset and a broad peak at 51 eV, and (iii) a quasi-linear region extending to more than 250 eV above threshold (Fig. 1). We associate the low-energy and linear regions with the two carbon atoms inside the perimeter of the molecule, while the mid-range region is linked to the atoms on the perimeter.

In the 10-eV resonance, the energy of the photon that has been absorbed is equal to the sum of the resonance energy and the energy required to promote two electrons to the DPI threshold. A theory for the origin of the low-energy resonance in pyrene is discussed in [6]. The approach is based on the Hubbard model [7], sometimes referred to as the Pariser-Parr-Pople model. The optical absorption associated with the two-site Hubbard Hamiltonian characterizes a process where a \(\pi\) electron is transferred to the site that is already occupied by a \(\pi\) electron with opposite spin. It consists of a single peak at the energy \(E_{OA}\) where

\[
E_{OA} = \frac{U}{2} + \left[\left(\frac{U}{2}\right)^2 + 4t^2\right]^{1/2}.
\]  

Here \(t\) denotes the transfer integral characterizing the interaction between \(\pi\) electrons on

FIG. 1: Relative DPI yield \(R\) as defined in Eq. (1) in pyrene as a function of excess energy. The solid line connects the data points. Corresponding error bars are given in [4]. See text for details.
nearest-neighbor sites and \( U \) is the electrostatic interaction between two \( \pi \) electrons on the same carbon site. In order to calculate the location of the DPI peak, we take parameter values appropriate for benzene: \( U = 10 \text{ eV} \) and \( t = 2.5 \text{ eV} \) \cite{9} and obtain the result \( E_{OA} = 12 \text{ eV} \), in reasonable agreement with experiment.

An alternative interpretation of the low-energy resonances in pyrene and coronene is outlined in \cite{2}. As discussed there, the peak is identified as a pairing resonance having a de Broglie wavelength of 2.8 Å, i.e. twice the C-C distance.

The linear behavior of the DPI shown in Fig. 1 resembles the linear behavior in pyrrole and the related molecules furan and selenophene \cite{4}. These molecules consist of a five-member ring with four carbon atoms and an impurity site occupied by an oxygen atom (furan) or selenium atom (selenophene), and in the case of pyrrole, a nitrogen-hydrogen complex. The effect of the impurity atom in these systems is to interrupt the periodicity associated with a ring of carbon atoms by replacing the ring with a linear array. In pyrene, the linear region is associated with the two interior carbon atoms. The linear behavior of the DPI in pyrrole and similar molecules is characteristic of a coherent process where the two photoelectrons are emitted simultaneously with equal kinetic energies and oppositely directed momenta \cite{5, 10, 11}. According to our interpretation, a similar process takes place in pyrene.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig2.png}
\caption{The relative perimeter pairing yield \( R' \) in pyrene vs excess energy. The data are obtained by subtracting the linear part of the ratio curve \( R \) shown in Fig. 1 extrapolated down to zero.}
\end{figure}

The mid-range region in pyrene reflects a continuum resonance that is likely to be related
to the pairing of two mobile electrons in a one-dimensional periodic potential \[12\]. In our analysis, the π electrons involved in the resonance are associated with the 14 carbon atoms on the perimeter of the molecule. In Fig. 1 there is a region where the resonance and the linear DPI-mechanism overlap. Assuming the contributions from the two processes superpose incoherently, we can extrapolate the linear curve to zero, thus obtaining an onset energy of 61 eV. Subtracting the linear response from the DPI data we obtain a plot of the perimeter resonance structure with an onset at 30 eV, a peak at 50 eV, and the upper cut-off at 75 eV (Fig. 2).

III. CORONENE

FIG. 3: Relative DPI yield $R$ as defined in Eq. (1) in coronene vs excess energy. Note the peak at 10 eV and the two pairing resonances at higher energies.

It is useful to compare the DPI results for coronene \[3\] with the corresponding pyrene data. Like pyrene, coronene has a 10-eV peak, which we attribute to an excitation involving the six carbon atoms in the interior. Unlike pyrene, there is no linear behavior at high energies. Instead, coronene has two regions of resonance structures, 30 to 70 eV and 80 to 125 eV (Fig. 3). The low-energy region qualitatively resembles what is found for the perimeter resonance in pyrene. We attribute the high-energy region to a pairing resonance involving the six interior carbon atoms. In Fig. 4 we display the upper pairing resonance on a larger scale. The width of the resonance, 45 eV, is comparable to the width of the
resonance in benzene, 40 eV [10].

In Figs. 2 and 3 the contribution to the DPI from the perimeter pairing resonance is approximately symmetric. There is, however, a significant asymmetry in the high-energy pairing resonance. These results suggest that the asymmetry is related to the number of carbon atoms in the closed loop. When the number is comparatively large, as in the perimeters of pyrene and coronene, the resonance is nearly symmetric with respect to the mid-point; when the number is small, as in the interior resonance in coronene, there is greater spectral weight below the midpoint.

IV. DISCUSSION

In order to test our model of independent subsystems, we turn now to anthracene ($C_{14}H_{10}$), which has the same number of perimeter atoms as pyrene but no interior atoms. In Fig. 5 we display the reduced resonance peak in anthracene that is obtained after subtracting the knock-out as well as the linear contribution to the DPI ratio. This resonance resembles the benzene resonance extending from 30 eV to approximately 90 eV above threshold with a peak at ca. 45 eV. It also resembles the mid-range resonance in pyrene (cf. Fig. 2) and is similar to the mid-range resonance in coronene (cf. Fig. 3). Taken together, these results support the hypothesis of independent DPI contributions from interior and perimeter carbon.
atoms.

Finally, we comment on treating the perimeter carbon atoms and the interior carbon atoms as independent subsystems. The justification for this approximation is associated with Hückel’s Rule, which predicts a high stability of an aromatic hydrocarbons for

\[ N = 2 + 4n, n = 0, 1, 2, \ldots \] (3)

where \( N \) is the number of \( \pi \) electrons (i.e. carbon atoms) in the planar ring \[14\]. Although neither pyrene nor coronene satisfy the rule when \( N \) is the total number of carbon atoms, the rule is satisfied for the perimeter subsystem and the interior subsystem in both molecules. The increased stability associated with Hückels Rule suggests the subsystems are likely to act quasi-independently in DPI processes.

V. SUMMARY

We have analyzed the DPI yield in the aromatic hydrocarbons pyrene and coronene. In both molecules, there are perimeter and interior carbon atoms. The results of our analysis show that the dominant features in the yield are independent contributions from the perimeter and interior subsystems. It is proposed that the quasi-independence of the two subsystems is due to the interior and perimeter subsystems independently obeying Hückel’s Rule.
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