Double photoionization of thiophene

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Abstract. The emission of two electrons from the valence shell of an atom or molecule by a single photon is due to electron correlation. This so-called double photoionization process has been studied extensively for atoms and smaller molecules using different experimental techniques. Here, we discuss double ionization of aromatic hydrocarbons using monochromatized synchrotron radiation over a wide range of photon energies in combination with the ion time-of-flight technique. In particular we will discuss the case of thiophene (C₄H₄S), which is a molecule of pentagonal structure similar to furan and selenophene.

1. Introduction

Simultaneous excitation of two electrons in He, Ne and Ar has been investigated 50 years ago by Madden and Codling [1] in the first gas phase experiment using synchrotron radiation. Four years later, Carlson [2] reported the first observation of a “double electron ejection” from the outermost shell of an atom using an X-ray tube. These investigations initiated a host of experiments on double photoionization with synchrotron radiation, in which two electrons are excited into the continuum by a single photon. Naturally, He became the textbook example for this process and many investigations using various techniques followed (see, e.g., [3]).

By the mid 1990s the ratio of doubly to singly charged He ions was settled and agreement between experiment and theory has been achieved. Investigations on Li, Be and Na demonstrated that the photon-energy dependence of that ratio is very similar to the one for He if the energy axis is in units of the energy difference between the corresponding double- and single-ionization thresholds [4]. Other elements, such as K and Mg, confirmed this observation, and even double K-shell photoionization exhibits the same energy dependence of the ratio as valence double photoionization. However, it was unclear whether this rule holds for molecules or not. An investigation on C₆₀ demonstrated that the double-to-single photoionization ratio is affected by the structure of the molecule [5]. If the initially emitted photoelectron has a kinetic energy that corresponds to a de Broglie wavelength that matches a geometrical distance in the C₆₀ molecule, so that a standing wave can be formed, then the electron stays longer in the molecule and increases thereby the probability for double ionization. Thus, the double-to-single photoionization ratio of C₆₀ shows local maxima at certain energies that correspond to a de Broglie wavelength equal to the diameter of the molecule, or the diameter of a hexagon formed by the carbon atoms, or the distance between two adjacent carbon atoms.

The C₆₀ experiment indicated that the structure of a molecule can affect the double-photoionization process. Therefore, we extended our research to aromatic hydrocarbons to see how the physical structure of a molecule affects the double-photoionization ratio. Experiments
on acenes, chains of one to five benzene rings, demonstrated the existence of at least three different double-photoionization mechanisms [6]. One of them, already known from atoms, is the “knock-out” mechanism, in which the photoionized electron knocks out a second electron while leaving the molecule. The knock-out model has been introduced by Samson [7] based on the similarity of the excitation-energy dependence between the double-to-single photoionization ratio of an atom and the electron-impact cross section of the corresponding singly charged ion. In the case of the acenes, the ratio of doubly to singly charged parent ions rises linearly with the length of the molecule [8]. The second double-photoionization mechanism in acenes is the brief formation of a Cooper pair that breaks up into two individual electrons after photo emission [9]. This mechanism, however, does not exist for the aromatic molecules with a pentagonal structure such as pyrrole, furan and selenophene. The third mechanism observed for aromatic molecules leads to a linear increase of the ratio above a certain photon energy. At higher energies this ratio starts to increase even faster than linearly.

Here, we report of our results for thiophene (C₄H₄S), which is an aromatic molecule similar to furan and pyrrole. Therefore, we expected a similar photon-energy dependence of the ratio. However, thiophene exhibits a surprising and unexplained deviation from the typical photon-energy dependence.

2. Experiment

The experiment was performed on the 6-meter toroidal-grating monochromator (6m-TGM) beamline [10] at the Synchrotron Radiation Center (SRC) in Stoughton, WI (USA) using photon energies from 18 to 170 eV. Briefly, the monochromatic photon beam entered through a differential pumping stage into the interaction region inside the vacuum chamber, where the photon beam crossed an effusive beam of thiophene molecules. A pulsed electric field accelerated the photoions and photofragments towards a drift tube with a Z stack of microchannel plates at its end. More details regarding the experiment and data analysis can be found in [6]. We have detected doubly and singly charged molecular parent ions of thiophene (C₄H₄S) that are stable or long-lived metastable parent ions. While fragments are clearly visible in our ion spectra, they are not considered here.

3. Results and discussion

Figure 1 shows an ion time-of-flight spectrum with the doubly and singly charged parent ions and fragments. Sulfur has four stable isotopes with the strongest one accounting for about 95%. In order to reduce errors we analyzed only the strongest peaks corresponding to the most abundant isotope. The peak of the doubly charged parent ions is well separated and its area was numerically integrated after background subtraction. The region near the singly charged parent ion (80-87 Da) exhibits the existence of other (much less abundant) isotopes as well as
fragmentation (loss of a hydrogen atom). Therefore we determined the area of the singly charged parent ion containing the main sulfur isotope by a least-squares fit using a Gaussian profile.

![Diagram](image)

**Figure 2.** Ratio of doubly to singly charged parent ions of thiophene as a function of photon energy (full circles). The full line is a fit curve to the data (see text for details).

The ratio of the doubly to singly charged parent ions in the threshold region is shown in figure 2. We applied a least-squares fit to the near-threshold data using a power function:

\[ R_s(h\nu) = a(\hbar\nu - E^{2+})^n + b. \]

(1)

Here, \( h\nu \) is the photon energy, \( E^{2+} \) the threshold energy, \( a \) a fit parameter, \( n \) an exponent and \( b \) an additional offset. This empirical method to determine the double-ionization threshold has been used in the past and was referred to as the “nth power rule” [11] meaning an approximately parabolic fit for double ionization. A small offset \( b \) was included in the fit function to take care of any remaining doubly charged ion signal due to second-order light or scattered light. The threshold energy obtained for thiophene is \((24.6 \pm 0.5) \text{ eV}\), which is similar to the energies for pyrrole \([24.20(6) \text{ eV}]\), furan \([25.18(14) \text{ eV}]\) and selenophene \([24.17(24) \text{ eV}]\) [6].

In figure 3 we compare the ratios of doubly to singly charged parent ions of pyrrole [9], furan [9] and thiophene. The pyrrole data are divided by 1.73 and the furan data are multiplied by 1.5 for an easier comparison. At photon energies up to about 50 eV the ratios show a very similar photon-energy dependence that can be modelled by scaled He ratio data [12] shown as a gray broken line. This line represents the “knock-out” mechanism that contributes to the creation of doubly charged ions dominantly at lower energies but will continue to contribute also at higher energies [9].

At about 50 eV photon energy we see a linear increase of the ratio similar to the ratios for pyrrole and furan. The linear increase of the ratio extends over a rather large energy range of 35 eV for thiophene up to 100 eV for furan. For thiophene, however, the ratio decreases again above about 88 eV before the energy is high enough to photoionize a sulfur 2p electron near 165 eV when Auger processes start to contribute predominantly to the double-to-single photoionization ratio. The rather abrupt kink in the ratio of thiophene near 88 eV is surprising and cannot be explained right now. After subtracting the contribution to the ratio from the knock-out mechanism, we obtain the data represented by open circles in figure 3. These data indicate that the thiophene ratio is actually not decreasing but remains virtually constant up to about 150 eV where the S 2p threshold may start to affect the ratios.

4. Summary

Although the aromatic molecules pyrrole, furan and thiophene have a very similar (pentagonal) structure, the linear increase of thiophene’s ratio does abruptly stop at 88 eV and remains essentially constant in contrast to the other molecules. This peculiar behavior of the thiophene ratio is not yet understood and will be explored in future experiments.
Figure 3. Ratios of doubly to singly charged parent ions of thiophene (red), pyrrole (purple) [9] and furan (green) [9] as a function of photon energy (data points with error bars connected by a full line). The ratios are scaled for easier comparison. The straight full lines emphasize the linear increase of the ratios for each molecule. The open circles are the thiophene data after subtracting the gray broken line.

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