First observation of a Fano profile following one step autoionization into a double photoionization continuum


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Abstract: We have measured the double photoionization cross section of sodium atoms between the first $2s^2 2p^6 2p$ double photoionization (52.4 eV) and $2s$-single $1.3s$ photoionization thresholds (71.0 eV). We have also observed a Fano profile into the double ionization continuum resulting from the interference between the one-step direct double photoionization process and the resonant double Auger decay of core-excited neutral sodium in the $2s + 3p$ resonance region. Profiles of absolute partial and total cross sections have been obtained in all important channels. The Fano and Starace parameters, in particular a width of 0.23 eV, have been determined, allowing full characterization of the resonance.

1. INTRODUCTION

Double photoionization in the outer shell of atoms has long attracted considerable interest, because it provides a sensitive test for the importance of electron-electron correlation effects. Early works on the rare gases, [1-4] and on some atomic vapors, [5-8] measured the energy dependence of the branching ratio between double and single photoionization cross sections. They found that double photoionization is not a rare event and provides the material for a critical test of atomic calculations. Many Body Perturbation Theory has been used at that time to calculate double photoionization cross sections.[9, 10] Agreement with the first experimental data available was reasonably good for the simplest rare gases, in particular for helium.[11]

Over the past ten years, the study of double photoionization processes has been extensively developed, owing to the dramatic improvements achieved in the intensity of monochromatic beams of synchrotron radiation (SR) available with newly built dedicated storage rings. Special emphasis was put on two electron processes, including double photoionization. [12-14] In particular, special attention was paid to the threshold[15-23] and high energy [24-27] behaviors of the double photoionization cross section, mostly in the rare gases. More recently, some results have been obtained in the study of energy- and angle-resolved double photoionization, measuring for the first time coincidences between both electrons ejected in the double photoionization processes, in krypton [28] and in helium.[29] Following this intense experimental activity, considerable progress has also been made in the theoretical description of the process, in particular for helium [30, 31] and sodium [32] atoms.

When the primary vacancy occurs in the inner-shell of an atom by photoabsorption of a single photon, doubly charged ions can be produced as the result of two different mechanisms. In the one-step double photoionization process, a second electron is simultaneously ejected from the outer shell via correlation effects.[9] In the two-step process [12-14, 33], the ejection of the first electron is followed by Auger decay of the singly charged ion. In the double Auger decay, the excess energy is distributed between two electrons that are simultaneously ejected from the singly charged ion, leading to triply charged ions. Experimental evidence for direct double-photoionization processes [34] and for double Auger decay [35, 36] was found many years ago.
2. THE SODIUM CASE

Alkali-atoms are unique candidates to study multiple ionization processes following inner-shell photoexcitation/ionization, because of their specific electronic structure. Among them, sodium is the most favorable case, owing to various theoretical and experimental considerations. The energy level diagrams of Na, Na$^+$ and Na$^{2+}$ are schematically shown in Figure 1, up to 71 eV energy above the ground state. Single ionization of neutral sodium in the 3s-, 2p-, and 2s-subshells requires 5.14 eV, 38.0 eV, and 71.0 eV, respectively. The first double ionization threshold, involving simultaneous removal of the outer shell 3s and first inner-shell 2p electrons occurs at 52.4 eV, according to: $2s^22p^6 + e^- + 2p^6 + e^-$. This means that, between 52.4 eV and 71.0 eV energy, the two-step Auger route cannot occur. Thus, only one-step double photoionization involving the simultaneous ionization of a 2p-inner electron and of the outer electron can produce doubly charged ions in this energy range. At 66.6 eV and above, there are discrete core-excited states forming Rydberg series converging to the 2s-ionization thresholds ($2s^22p^5 + e^- + e^-$). These autoionizing states are accessible by photoexcitation of a 2s-electron according to: $2s^22p^5 + 2s^4 + e^- + e^-$. Earlier photoabsorption measurements, [65] have observed and identified the first members of the series. These excited states lie above the first $2s^22p^5 + 2P_1/2, 3/2$ double-ionization thresholds, but below the next inner-shell single ionization and the second double ionization ($2s^22p^5 + e^- + e^-$).

In the work presented here, we have measured the relative abundance of Na$^+$ and Na$^{2+}$ ions produced between 52.4 eV and 71 eV photon energy. At 66.6 eV, the excited $2s^22p^5 + 2P_1/2, 3/2$ double-ionization threshold, at 71.0 eV [64], respectively.

![Fig. 1 - Simplified energy level diagram of neutral, singly-, and doubly-charged atomic sodium.](image-url)
interfer on resonance with the resonant double Auger process (also called resonant double 
autoionization). All other relaxation schemes lead to singly charged final states of Na\(^+\) ions. In Figure 1, 
we have represented three of them that can also be reached by direct photoionization from the ground 
state of atomic sodium: 2s\(^2\)2p\(^5\)3s \(^1\)P, with only one 2p-electron being removed, corresponding to the 
“main line” in a photoelectron spectrum; 2s\(^2\)2p\(^3\)3p \(^2\)P with the outer 3s-electron being simultaneously 
excited onto a 3p-orbital via continuum state interaction (the excited electron has changed its orbital 
quantum number by one unit), corresponding to the so-called “conjugate shake up” satellites (CSU); and 
the 2s\(^2\)2p\(^3\)4s \(^1\)P states, with the 3s-electron being simultaneously excited onto a 4s-orbital via a 
monopole transition (the excited electron does not change its orbital quantum number), corresponding to 
shake up satellites (SU). In a previous work, \[66\] photoelectron spectra of sodium have been recorded at 
many photon energies in the same photon energy range, showing strong variations of the relative 
intensity of some of the photoelectron lines in the energy region of the resonance. Using these previous 
data and the newly obtained results, we have been able to determine absolute values of the partial 
photoionization cross sections by normalization to the absolute photoabsorption cross section, to 
determine the Fano parameters of the resonance in the total photoabsorption cross section \[67,68\], and to 
analyze with the Starace’s formulation \[69\] the line profiles in the different ionization channels, in 
particular in the double photoionization channel that shows a characteristic Fano profile.

3. EXPERIMENT
SR from the BESSY storage ring was used between 50 eV and 71 eV to analyze the ratio of Na\(^{++}\) and 
Na\(^+\) ions produced by photoionization. A schematic view of the experimental set up is shown in Figure 2. 
The light emitted from a bending magnet of BESSY was monochromatized by a toroidal grating 
monochromator (TGM) with a relative resolution \(\Delta h/v/\nu = 4 \times 10^{-3}\). Closing the TGM slits to a width of 
300 \(\mu\)m and using a 950 lines/mm grating, the photon flux was \(\approx 4 \times 10^{10}\) photons/second in a band pass 
of 0.3 eV at 65 eV photon energy and for 100 mA electron current in the ring. To suppress higher order 
contributions to the monochromatized light, we mounted an aluminum foil of 100 nm thickness into the 
beam. The monochromatized light was focused into the interaction zone of a time-of-flight-ion-mass 
analyzer (TOF) where it crossed a beam of Na atoms generated inside a resistively heated furnace. Ions 
produced by photoionization were extracted and accelerated into the drift section of the TOF by 
electrostatic pulses of 300 V amplitude, a pulse length of typically 2 \(\mu\)s and a pulse frequency of 25 kHz. 
Measuring the time of flight of the ions between interaction zone and detector, a separation in regard to 
the ratio of mass and charge was possible.

A typical TOF ion spectrum, measured at 60 eV photon energy, is shown in Figure 3 Numerous ionic 
lines appear, partly due to photoionization of the residual molecular gases by SR. However, the most 
intense signal is the Na\(^+\) ion line around channel number 2500. Near channel number 1700, one observes 
also a very small signal that can be identified as a Na\(^{++}\) ion line produced by direct double 
photoionization of Na atoms.

Fig. 2- Scheme of the experimental set up used for the photoion spectrometry measurements described 
in this work (see text for detailed explanation).

For a large number of photon energies, the ratio of Na\(^{++}\) and Na\(^+\) intensities was measured from spectra 
similar to the one shown in Figure 3. After that proper instrumental corrections, mainly for the ion 
detector efficiency, have been applied, the relative cross section for formation of Na\(^{++}\) ions was obtained 
as a function of photon energy. The detailed experimental procedure will be given elsewhere. \[70\]
4. RESULTS

Figure 4 presents the relative cross section for double photoionization of atomic sodium as a function of photon energy between the double ionization threshold and the single 2s-inner shell ionization thresholds. The data points have been extracted from the Na\(^{++}/Na^+\) ratios measured at different photon energies. As expected, no Na\(^{++}\) signal was observed below 52.4 eV and the double photoionization cross section starts from zero at threshold. Since, between 52.4 eV and 71.0 eV, only direct double photoionization (shake off) contributes to the production of Na\(^{++}\) ions outside of the 2s \(\rightarrow\) np resonance energies, the cross section between 52.4 eV and 71.0 eV for the \(2s^22p^53s + h\nu \rightarrow 2s^22p^5 + e^- + e^-\) shake off process can be read directly from Figure 4 to increase from 0 to about 1% of the total single photoionization cross section. The sudden increase in the Na\(^{++}\) ion formation at 71.0 eV was also observed, since normal Auger decay of a 2s-vacancy ends up in the Na\(^{++}\) ground state.

Let's turn now to the apparently weak Fano-type structure at 66.6 eV, indicating a strong coupling of the shake off process to the corresponding 2s \(\rightarrow\) 3p resonance. First of all, since the resonant state is an excited state of the neutral atom, only the double resonant Auger process can contribute to the decay of this excited state into the doubly ionized \(2s^22p^5\) \(2p_2\) \(2p_3\) final states. In addition, this process seems to interfere with the direct one-step double photoionization, suggesting that the intensity of both processes is in the same order of magnitude. In previous work dealing with decays of core-excited resonances, the direct shake off process was negligible compared to the resonant process, precluding the observation of any Fano-type profile similar to the one observed here. In order to establish a valuable comparison with the effect of the resonance into the singly ionized channels, we recall in Figure 5 an example of the results that have been previously obtained using photoelectron spectrometry for two of the singly ionized final states of Na\(^+\) in the same energy region [66]. The branching ratios shown in this figure were determined by measuring a large number of photoelectron spectra in the photon energy range of interest, i.e., the CIS (constant ionic state) method was not used. Variations of the incident photon flux were monitored by measuring the integrated area under the 2p-photoelectron line of neon atoms simultaneously introduced in the source volume of the cylindrical mirror analyzer used to energy analyze the photoelectrons (CMA). [66] The variation of the Na atoms density as a function of time was also systematically checked by measuring periodically the same photoelectron spectrum at a given photon energy. Possible changes of this density were accounted for. In the upper part of the figure, one sees the branching ratio for the shake up satellite intensity (2s\(^2\)2p\(^5\)4s / 2s\(^2\)2p\(^5\)3s), and, in the lower part, the branching ratio for the first conjugate shake up satellites (2s\(^2\)2p\(^5\)3p / 2s\(^2\)2p\(^5\)3s). The branching ratio is apparently enhanced on resonance by a factor 2.8 in the CSU channel and by a factor 1.5 in the double ionization channel. One does not observe a strong effect in the SU channel. In Table I, we have summarized the values of the branching ratios measured off and on resonance in all observed channels, including the single ionization channel. Note that every feature observed in photoabsorption measurements [65] is also observed here, especially in the CSU branching ratio. The second resonance of the series, 2s \(\rightarrow\) 4p, at 69.3 eV photon energy, has also some effect in this channel.

Branching ratios into the different final state channels is an interesting parameter to know. However, a true comparison of relative intensities and profiles can be made only on the energy dependence of the absolute partial photoionization cross sections. This will be the subject of the next paragraph.
Table I. Branching ratios for photoionization of Na into the various final state channels off resonance and at 66.6 eV resonance energy (2p^53s channel = 100).

<table>
<thead>
<tr>
<th>Final state</th>
<th>Off resonance</th>
<th>On resonance</th>
<th>Enhancement factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>2s^22p^53p</td>
<td>12</td>
<td>33</td>
<td>2.8</td>
</tr>
<tr>
<td>2s^22p^54s</td>
<td>16</td>
<td>19</td>
<td>1.2</td>
</tr>
<tr>
<td>2s^22p^54p</td>
<td>2</td>
<td>5</td>
<td>2.5</td>
</tr>
</tbody>
</table>

5. DISCUSSION

We have established all partial cross sections on the same relative scale using photoion and photoelectron spectrometries. Then, we determined the absolute scale of the cross sections by normalizing, at 64 eV photon energy, i.e., on the low energy side of the 2s \(\rightarrow\) 3p resonance, the relative cross sections to the absolute photoabsorption cross section as measured by Codling et al.[71]. This is possible only when all photoionization channels have been previously analyzed.

Let's discuss first the total photoabsorption curve in the energy region of the 2s \(\rightarrow\) 3p resonance obtained by adding the contributions of our partial cross sections determined into the different ionization channels. The resulting curve is shown in Figure 6 as points with error bars. The error bars take into account the errors in determining the branching ratios, including corrections due to variation of the photon flux and possible changes in the atomic density. Like for all data presented in this paper, the overall uncertainty on the absolute value of the total photoabsorption cross section used for normalization is not included. Absolute values of the partial cross sections would of course be affected if the normalization point would change, but not the shape neither the parameters of the partial cross sections in the region of the resonance.

Note that the values of the cross section on the low energy side of the resonance are 15% to 20% higher, in comparison to the value of the cross section at the top of the 2s \(\rightarrow\) 3p resonance, than in the data of Wolff et al.[65]. In fact, these authors have measured only the relative shape of the absorption spectrum. The fact that the 2s \(\rightarrow\) 3p resonance appears with a better contrast in the measured photoabsorption curve than in the reconstructed curve might be attributed to the better resolution of the photoabsorption data, \(\equiv 0.01\) nm against about 0.03 nm in our work.

5.1 Fano parameters for the total photoabsorption cross section.

According to Fano, [67, 68] the total photoabsorption cross section \(\sigma_{tot}\) for the case of an isolated resonance interacting with several continua states can be parametrized in the following form:

\[
\sigma_{tot} (E) = \sigma_0 (E) \left[ \rho^2 (q + \epsilon)^2 / (1 + \epsilon^2) + 1 - \rho^2 \right]
\]

with:

\[
\epsilon = (E - E_0) / \Gamma / 2
\]

where the Fano parameters \(q\) (profile index) and \(\rho^2\) (correlation coefficient) are assumed to be constant over the resonance, \(\sigma_0 (E)\) gives the nonresonant cross section, \(\Gamma\) and \(E_0\) are the width and the energy of the resonance, respectively. \(q\) and \(\rho\) can be expressed as a function of the wavefunction of the ground and final states.[67, 68]

In order to extract the true resonance parameters from the experimental data, a deconvolution of the experimental photoabsorption cross section with the monochromator band pass function must be performed. However, rather than using such a deconvolution, the true resonance profile (generated from the parameters \(E_0\), \(\Gamma\), \(q\) and \(\rho^2\)) was convoluted with the monochromator band pass function (a Gaussian
profile with 0.31 eV FWHM) and then compared with the experimental data by a least-squares fit. For this purpose, a linear behavior of the nonresonant cross section \( \sigma_0 \) was assumed and none of the parameters was a priori kept fixed. Starting values to inject into the fitting procedure were extracted directly from the experimental data. The procedure was repeated systematically, the \( \chi^2 \) values providing the criterion to select the best set of resonance parameters. Table II lists the final values of the resonance parameters determined in that way, using Mathematica software. Codling et al. [71] have estimated a \( q \)-value of -2 (±0.5), in agreement with previous estimations by Wolff et al.[64] Our determination is more accurate, and confirms the validity of the first estimations. The width of the resonance \( \Gamma \), 0.23 eV, is significantly smaller than previously estimated by Codling et al. on the basis of a \( q \)-value of -2. It is interesting to compare our value with a completely independent determination of the widths of the transitions: \( 2s2p^63^S \rightarrow 2s2p^52p_{1/2},3/2 \) in Na by Breuckman et al.[72]. Studying the Auger spectrum of Na produced by electron impact excitation, they measured, for both \( 1^3S \rightarrow 2p \) transitions, widths of 0.24 (2) eV, in excellent agreement with our determination since the widths of these different transitions is mainly governed by the natural width of the 2s-hole.

Our value of 0.23 eV for the width of the \( 2s2p^53s3p \) \( 2p \) state is equivalent to an autoionization lifetime of \( 2.9 \times 10^{-15} \) sec, i.e., about twenty times less than that of the \( 2s2p^53p \) state in Ne measured long time ago by Madden and Codling.[73] This is qualitatively understandable since, in the case of neon, only one channel, the \( 2s2p^5 2p_{1/2},3/2 \) channel, is accessible to autoionization, while many more channels, including the double photoionization channel, are open in the case of the \( 2s2p^53s3p \) \( 3p \) state in sodium.

The oscillator strength \( f \) of the \( 2s \rightarrow 3p \) transition can also be deduced from our experimental measurements, since it is related to the Fano parameters by the expression:

\[
g f = 0.195 q_2 \rho^2 \sigma \Gamma
\]

where \( g \) is the statistical weight \( 2J + 1 \), \( \sigma \) is expressed in megabarns, \( \Gamma \) is measured in Rydbergs. With the values given in Table II, we obtain \( f = 1.7(2) \times 10^{-3} \), a value almost identical to the oscillator strength of the \( 2s \rightarrow 3p \) transition in neon similarly determined.[73] This equality confirms once more that correlation effects between the core and the outer electrons in sodium have little influence on the inner-shell photoexcitation spectra.

5. 2 Partial cross sections

Absolute values of the partial cross sections were determined using the same normalization as for the total photoabsorption cross section. They are shown in Figure 7 for the three most important continuum channels studied in this work, i.e., from top to bottom, the CSU channel, the double ionization channel and the single \( 2p^1 \) photoionization channel. Note the quite different ordinate scales for each of the three panels. The experimental values are the points with error bars. The overall error on the total photoabsorption cross section used for normalization, 20% to 25%, is not included in the values of the partial cross sections. Interestingly enough, strongly different profiles appear on resonance in the various continua. In the CSU channel, the cross section has an almost lorentzian profile, as it was already evident in the figure showing the branching ratios, confirming that little interference occurs between the weak direct process and the strong indirect resonant process. This is not the case in the single \( 2p^1 \), and, even more, in the double photoionization channels where one observes two similar Beutler-Fano profiles, although the absolute values of the cross sections are strongly different in both continua. Since the first observations in single photoionization of helium [74], many Fano profiles have been observed [14, 75-78] in single photoionization channels, but it is the first time, to our knowledge, that such a profile is directly observed following a one-step decay of a neutral core-excited state into a double photoionization continuum. Related measurements are the recent observations of Auger transitions contributing to valence double photoionization [79], and of asymmetric photoelectron line profiles [80, 81] in inner-shell shake up satellites lying above the double ionization threshold involving less bound electrons, suggesting a coupling between discrete satellite states with underlying shake off continua.

In Figure 7, the solid lines are the result of a fitting of the experimental data to theoretical formulations including several parameters. Theoretical expressions for the behavior of partial cross sections within a resonance have been formulated by Starace [69], in a form analogous to the Fano formula describing the behavior of the total cross section in the neighborhood of an isolated resonance. The expression for the partial cross section in the observable photoemission channel \( \mu \) at energy \( E \) is given, as a function of the
Fano q parameter and the real and imaginary parts of a new parameter $\alpha (\mu, E)$, according to:

$$\sigma(\varepsilon) = \sigma_0 (\varepsilon) \frac{C_1 + C_2 \varepsilon + \varepsilon^2}{1 + \varepsilon^2}$$

with:

$$C_1(\mu, \varepsilon) = 2 \left[ q \text{Re} \langle \alpha_\mu \rangle - \text{Im} \langle \alpha_\mu \rangle \right]$$

$$C_2(\mu, \varepsilon) = 1 - 2q \text{Im} \langle \alpha_\mu \rangle - 2 \text{Re} \langle \alpha_\mu \rangle + (1 + q^2) |\alpha_\mu|^2$$

$\sigma_0 (\varepsilon)$ is a slowly varying nonresonant partial cross section. The complex parameters $\alpha_\mu$ are given by:

$$\alpha_\mu = \frac{\langle \Phi | V | \mu \rangle}{\langle g | T | \mu \rangle} \left[ \frac{2\pi}{\Gamma} \sum \mu < g \mu | T | \mu > < \mu | V | \phi > \right]$$

where $g$ represents the ground state, $\Phi$ is the final state, mixing discrete and continuum states, and $V$ is the Coulomb interaction. The summation extends over all photoionization channels $\mu$.

In Figure 7, the solid curves represent least-squares fit to the function $\sigma(\varepsilon)$ convoluted with the instrumental function describing the monochromator band pass. The same procedure was used as for the determination of $q$ and $\Gamma$ from the total photoabsorption cross section. All parameters, including $\Gamma$, were again treated as free parameters. The numerical results of the least-squares fit for each photoionization channel are given in Table III. The $\Gamma$ values deduced from the partial cross section measurements are equal to the one determined from the total photoabsorption cross section.

The single 2p$^{-1}$ and double 2p$^{-1}$3s$^{-1}$ partial cross sections have similar profiles, although their absolute values are widely different, by nearly a factor 70 off resonance, the intensity in the double photoionization continuum showing a larger fractional rise (1.5) than does the intensity in the single 2p$^{-1}$ photoionization channel (1.2). The CSU profile is slightly higher on the low energy side, but a symmetric Lorentzian curve will fit into within the experimental error. It has the largest fractional rise on resonance (2.8). The actual value is, in fact higher (\geq 4.5) because of instrumental broadening. The total cross section which receives about 70% of its intensity from the single ionization channel has a shape similar to the single photoionization cross section.

Fig. 7 - Partial photoionization cross sections for photoionization of atomic sodium into the CSU-, double- and single 2p$^{-1}$ photoionization channels, respectively (from top to bottom).
Table III. Fitting parameters for the partial cross sections

<table>
<thead>
<tr>
<th>Ionic state</th>
<th>$\Gamma$ (eV)</th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$\sigma_0$ (Mb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2s$^2$2p$^5$3s</td>
<td>0.23(1)</td>
<td>1.10(5)</td>
<td>-0.50(5)</td>
<td>7.2(4)</td>
</tr>
<tr>
<td>2s$^2$2p$^5$3p</td>
<td>0.230(5)</td>
<td>4.50(5)</td>
<td>-1.00(5)</td>
<td>0.84(5)</td>
</tr>
<tr>
<td>2s$^2$2p$^5$</td>
<td>0.230(5)</td>
<td>1.69(1)</td>
<td>-1.84(1)</td>
<td>0.082(5)</td>
</tr>
</tbody>
</table>

6. CONCLUSION

The use of both photoelectron and photoion spectrometries has been demonstrated to be necessary to characterize an isolated resonance interacting with several continua. The total photoabsorption and partial photoionization cross sections have been fully parametrized. The width of the 2s$^2$2p$^6$3s $^2S \rightarrow$ 2s$^2$2p$^5$3p $^2P$ resonance in Na has been accurately measured. The high sensitivity of ionic detection has provided the first direct observation of a Fano profile in a double photoionization continuum following one step autoionization, in spite of the weak strength associated with this channel, thirty years after the first observation of such a profile in the He$^+$ singly ionized channel.

7. REFERENCES


