Direct Double Photoionization Involving Inner and Outer Electrons: First Experimental Determination and Many-Body Calculations of an Absolute Cross Section

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(Received 24 May 1994)

Using synchrotron radiation, we have determined the absolute cross section for double photoionization involving the $2p$ and $3s$ electrons in atomic sodium. We have also calculated this cross section in the many-body perturbation theory approximation. Our experimental and theoretical results are in good agreement one with each other and represents the first absolute determination of a double photoionization cross section in the case where the two electrons belong to two different shells.

PACS numbers: 32.80.Hd, 32.80.Fb

In this Letter, we present the results of the first experimental determination of an absolute double photoionization cross section for the direct emission into the continuum of two electrons belonging to two different shells. These measurements were performed for simultaneous photoionization of $2p$ and $3s$ electrons in sodium atoms. We also present calculations of the double photoionization cross section of Na ($2p3s \rightarrow k_1k_2$) for photon energy from 50 to 250 eV, using many-body perturbation theory (MBPT).

Double photoionization (DPI) 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. Earlier work on the rare gases [1–4] revealed that the shakeoff theory, describing DPI as the result of monopole transitions resulting from relaxation of the hole state produced in the outer shell, was unable to account for most of the DPI intensity. MBPT was used at that time to calculate DPI cross sections in neon [5–7], helium [8], and argon [7]. Agreement with the first experimental data available was reasonably good, especially for helium [9]. Most recently, DPI has been extensively studied in the outer shell of the rare gases [10–18], owing to the increased performance of synchrotron radiation (SR) sources. In the measurements of the energy dependence of the branching ratio between double and single photoionization cross sections, considerable attention was given to the threshold [10–12] and high energy [13–15] behaviors of DPI. Some data have also been obtained in the study [16–18] of the energy and angle-resolved DPI process. Parallel to this experimental activity, progress has also been made in theoretical calculations of DPI cross section for helium [19–22] and for argon [23].

When the primary vacancy is produced in an inner atomic subshell, doubly charged ions can result from two different mechanisms. In the one-step DPI, a second electron is simultaneously ejected from the outer shell via correlation effects, namely [5–8] core relaxation (CR), ground state correlations (GSC), and inelastic scattering (IS) of the photoelectron in collision with outer shell electrons while leaving the atom. CR and IS can be grouped into the category of final state correlations (FSC), although such a classification should be considered with some caution, as it has been shown that it is gauge dependent [19]. In the two-step process [24], the ejection of the first electron is followed by Auger decay of the singly charged ion, leading to the emission of a second electron and to the production of a doubly charged ion. Recently, a large number of experiments have dealt with DPI following inner-shell photoexcitation or photoionization in the rare gases [24,25]. Electron and mass spectrometries have both been used [24], allowing one to measure the rate of doubly charged ions and to clearly identify the result of one-step and two-step processes, respectively. In most of the cases, the two-step process was found to dominate [24]. In atomic vapors, almost all experimental works have studied the two-step process following atomic core excitation [26], within a few exceptions [27–29]. Only branching ratios were measured, and no calculations or measurements of one-step DPI was carried out.

In the work presented here, we chose the example of sodium, because alkali atoms offer a special case, hav-

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ing a single electron in the outermost shell outside of a closed core, and because sodium atoms are the easiest of these atoms to handle in the vapor phase. Removing simultaneously one core electron from the first inner subshell, namely the $2p$ subshell, and the electron from the $3s$ outer shell, allows then an unambiguous assignment of the measured rate of Na^{++} ions produced in DPI at photon energies lower than the binding energy of the next inner threshold. Specifically, single ionization thresholds for photoionization in the $3s$, $2p$, and $2s$ subshells of atomic sodium are 5.14, 38.0, and 71.0 eV, respectively. The first DPI threshold, involving simultaneous emission of $2p$ and $3s$ electrons, is at 52.4 eV. Thus, between 52.4 and 71.0 eV all doubly charged Na^{++} ions measured by ion spectrometry are exclusively produced by the one-step direct mechanism, with the exception of the excitation energies of the $2s2p^6 3snp$ core-excited states [29–31] above 66.6 eV. Above 71.0 eV, combining electron and ion spectrometries allows us to discriminate one-step against two-step processes. Moreover, sodium is one of the very few atoms, in addition to the rare gases, where absolute partial cross sections can be experimentally determined from the partitioning [32] of the measured absolute photoabsorption cross section [30]. Thus, as for photoionization in the outer shells of the rare gases, our partial cross sections have been measured independently of any calculation, offering a valuable test of the many-body perturbation theory.

SR from the BESSY (Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung m.b.H) storage ring was used between 50 and 135 eV to analyze the ratio of Na^{++} to Na^{+} ions produced by photoionization. SR from the SuperACO (les Anneaux de Collisions du Laboratoire de l'Accélérateur Linéaire) storage ring in Orsay was used, in the same energy range, to measure the relative intensities of the photoelectron lines corresponding to the different singly charged final ionic states [33–35]. In Fig. 1, we show the branching ratios which have been determined for single photoionization in the $3s$, $2p$, and $2s$ subshells, photoionization accompanied by excitation in the $2p$ and $2s$ subshells [shakeup satellites (SU), "conjugate" shakeup satellites (CSU)], and the $2p^5$ Na^{++} DPI channel. The lines in Fig. 1 result from a polynomial fit of the experimentally measured branching ratios. The error on these branching ratios is at most 3% for the lowest intensity processes.

Absolute values of the $(2p, 3s)$ DPI cross section are given in Fig. 2. The error due to the partitioning of the total cross section is mainly the statistical error and is a few percent only. The main error on the absolute cross section comes from the inaccuracy on the total photoabsorption cross section [30], i.e., about 25%. It is not shown in Fig. 2. The experimental values are compared in the figure to the results of our calculations made using the MBPT.

While MBPT gives reasonably good results that provide understanding of measurements in closed-shell atoms

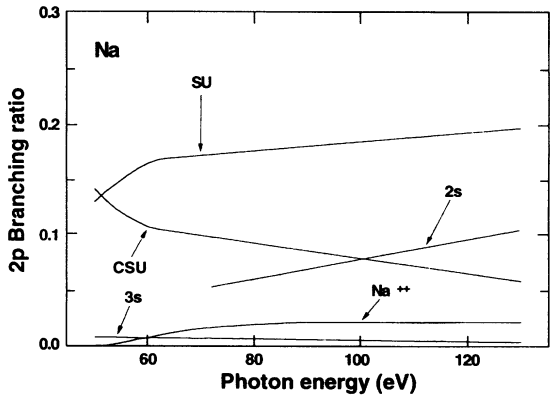

FIG. 1. Branching ratios for photoionization into the different single and double continuum channels. Data are normalized to the intensity of the $2p$ single photoelectron line.

[5–8,23], for open-shell atoms there remain a number of unanswered questions: (i) What is the relative importance of different processes involved in final and ground state correlations? (ii) What is the significant choice of potential to describe continuum wave functions of ejected electrons? (iii) How is the convergence in terms of the partial wave expansion employed in the calculation? Our calculation shed light on these questions.

In MBPT the final state wave function is described as an antisymmetric combination of two continuum $\phi k_1 m_{s1}$, $\phi k_2 m_{s2}$, and the remaining core orbitals, where $\phi k_i m_{si}$ $(i = 1, 2)$ is expressed as a partial wave expansion:

$$\phi_{km_s} = \frac{1}{k^{1/2}} \sum_{l=0}^{\infty} \sum_{m=-1}^{l} i^l e^{-i\delta_l} Y_{lm}^*(\hat{k})\, R_{\varepsilon kl}(r)\, Y_{lm}(r)\, \chi_{ms}\,, \tag{1}$$

where δ_l is a phase shift, Y_{lm} is a spherical harmonic, χ_{ms} is a spin function, and the radial part of the wave function

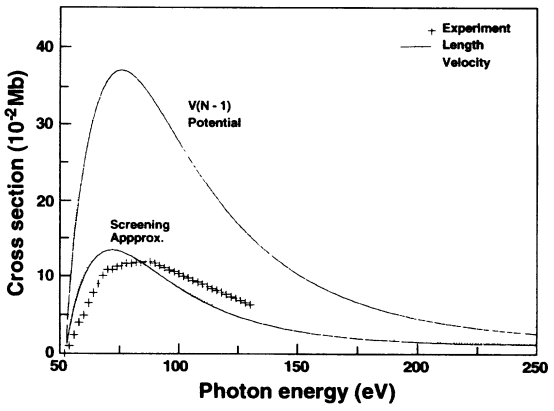

FIG. 2. Comparison of measurement and calculations for the total σ^{++} of $(2p, 3s)$ DPI of Na. Theoretical results are plotted for both dipole-length (solid curves) and dipole-velocity (dashed curves) matrix elements with two different choices of potential.

$R_{kl} = u_{kl}/r$ satisfies $h_0 u_{kl} = \varepsilon_k u_{kl}$ with, in atomic unit,

$$h_0 = -\frac{1}{2}\nabla^2 + \frac{l(l+1)}{2r^2} - \frac{Z}{r} + U(r). \quad (2)$$

The potential $U(r)$ is taken as

$$U = V_{\mathrm{HF}}^N + (1-P)\Omega(1-P), \quad (3)$$

where $P = \sum_{\mathrm{core}} |n\rangle\langle n|$ ensures orthogonality of excited and ground state orbitals, and Ω is an arbitrary Hermitian operator which is chosen to represent a desired physical situation [36]. If one takes $V_{\mathrm{HF}}^K = \langle\Psi_K|\sum_{i<j}(\mathbf{r}_i - \mathbf{r}_j)^{-1}|\Psi_K\rangle$, where K represents N, $N-1$, or $N-2$ electrons LS-coupled states, then the choice that $\Omega = V_{\mathrm{HF}}^{N-1} - V_{\mathrm{HF}}^N$ corresponds to the widely used V^{N-1} potential, and the choice that $\Omega = V_{\mathrm{HF}}^{N-2} - V_{\mathrm{HF}}^N$, i.e., V^{N-2} potential, will give asymptotic behavior in a double ionized environment to the continuum. Apparently the screening approximation, which means that one-ejected electron moves in a V^{N-2} potential and another in a V^{N-1} potential, will result in a physically more appropriate model Hamiltonian $H_0 = \sum_i h_0(r_i)$ than that chosen as both electron in the V^{N-1} potential. In fact, Carter and Kelly [7,8] proved that, by using the screening approximation, certain classes of higher order terms in MBPT canceled out, and the results from a low order calculation could provide reasonable agreement with experimental data. Here, the low order calculation for DPI means to include four basic diagrams of Figs. 3(a)–3(d), with correlation corrections to the dipole interaction of Figs. 3(e) and 3(f). Figures 3(a) and 3(b), and 3(c) and 3(d) represent final state correlations (FSC-I and -II) and ground state correlations (GSC-I and -II), respectively. Exchange diagrams are always understood to be included. Figure 3(e), a GSC to the dipole interaction, improves the agreement between calculations using the length and velocity form of the dipole operator, as will be shown, in Fig. 2. Figure 3(f), a FSC to the dipole interaction, takes into account interaction between different dipole transition channels.

The total cross section considered is the ejection of a combination of inner- and outer-shell $2p3s$ pair, leaving the $1s^2 2s^2 2p^5(^2P)$ core configuration. We evaluated the diagrams in Fig. 3 for 44 channels in the nine main final state configurations $klkl'$, from $ksks$ up to $kfkh$. Two sets of excited bounds and continuum orbitals were obtained using the V^{N-1} and V^{N-2} potential. For each l value in each basis set, 10 bound states and 56 continuum orbitals ranging from $k = 0.05$ to 16.6 were explicitly calculated. The DPI threshold is taken as the experimental result of 52.4 eV. For the single-particle energies, we used the self-consistent-field (SCF) values which are given by the difference between SCF solutions of Hartree-Fock equations for the residual ion and the ground state.

The calculated cross section $\sigma^{++}(h\nu)$ is compared in Fig. 2 with the experimental measurement for two cases: (1) using the V^{N-1} potential for both ejected electrons and (2) using the screening approximation. It is obvious that, by using the combination of V^{N-1} and V^{N-2} continuum orbitals, the low order MBPT is able to provide

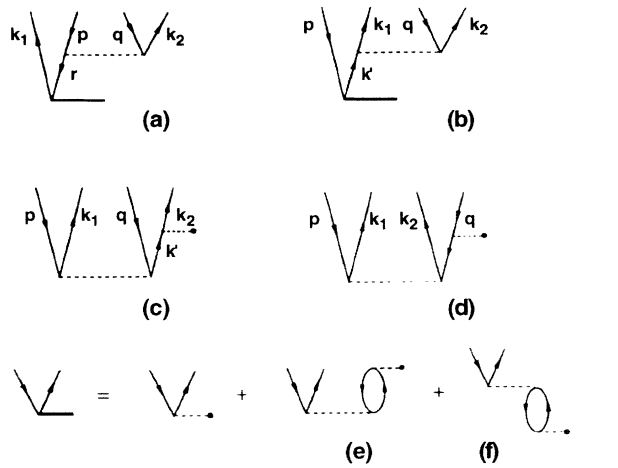

FIG. 3. MBPT diagrams calculated in this work for double photoionization of Na. Dashed lines ending with a solid dot indicate dipole interaction; other dashed lines represent Coulomb interactions. Solid lines with a downward arrow stand for core orbitals and solid lines with an upward arrow for excited virtual states or continuum orbitals. Exchange diagrams are understood to be included.

a qualitative description of DPI, since the agreement between measurements and calculations is spectacularly improved in the second case. The contributions for the nine $2p3s \rightarrow kk'$ channels have been calculated over the entire photon energy range. The dominant contributions come from $kskd$, $kdkd$, and $kpkf$ channels. The two types of final state configurations of $klk'l$ and $klk'(l+2)$ show a clear pattern of convergence. With the increase of l value, the calculated contribution decreases and moves toward the higher photon energy side. It is estimated that other high-l excitation channels neglected in the present calculation might contribute a 10%–15% increase to the total cross section. However, the rise of the total cross section near the threshold is much more rapid than the measured data, and it is not understood at present, although one may suspect an overestimation of the screening in using the V^{N-2} potential. Analysis of DPI amplitudes arising from FSC and GSC indicates that there is a delicate interference between the two types of correlation. As an example, the $2p3s \rightarrow kskd$ channel is shown in Fig. 4. FSC diagrams, including core relaxation and inelastic scattering, give the most substantial contributions, while GSC have a much weaker effect because the $3s$ electron is loosely bound. This result is different from the conclusions drawn on DPI from the same outer subshell in some rare gases, where the contribution of GSC has been found to be significant [6,8].

In conclusion, we have determined for the first time the absolute cross section for direct DPI involving one inner and one outer electron. The first MBPT calculations of this cross section already show good qualitative agreement with the experimental data. They confirm that final state correlations (CR and IS) bring by far the most im-

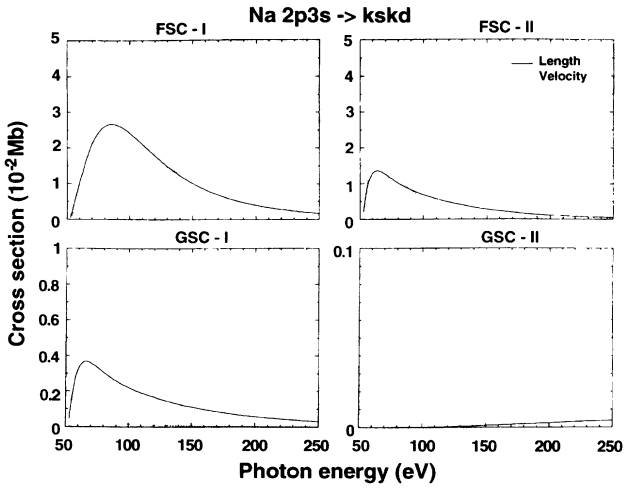

FIG. 4. Cross sections from individual diagrams of Figs. 3(a)–3(d) for Na $2p3s \rightarrow kskd$ transition.

portant contribution to DPI. They also demonstrate how important the choice of the potentials felt by the ejected electrons is.

The authors would like to thank W. R. Johnson, C. Pan, and J. J. Boyle for helpful discussions. The work at BESSY was supported by the Bundesministerium of Germany, the work at Orsay by the Centre National de la Recherche Scientifique. Z. W. L. and J. C. L. were supported in part by the U.S. National Science Foundation.

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