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Complete description of 3p photoionization in calcium

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Abstract. Within the dipole approximation and the LS-coupling limit 3p photoionization in atomic calcium is described completely by two matrix elements and one relative phase. These three parameters are extracted from experimental observables and compared with theoretical calculations (RRPA transformed to the non-relativistic limit) for photon energies around the Cooper minimum in the 3p $\rightarrow \epsilon$d channel. Taking into account the intensity-borrowing model, excellent agreement between theoretical and experimental data is found.

1. Introduction

Photoionization in closed-shell atoms leads, within the dipole approximation, to at most three transition matrix elements which then fully describe all photoionization observables. Since these matrix elements are complex quantities and the overall phase is irrelevant, one then needs to know at most five independent experimental observables in order to extract from the experimental data the magnitudes of these matrix elements and their relative phases. An experiment which provides the maximum information about the underlying process in these matrix elements and phases has been referred to as a ‘complete’ or ‘perfect’ experiment (Fano 1957, Bederson 1969a, b, Kessler 1981). The first complete experiment in photoionization was reported by Heinzmann (1980a, b): the partial photoionization cross section, the angular distribution parameter and three spin-polarization parameters of the emitted photoelectrons were used to derive from these observables for $5p_{3/2}$ (and $5p_{1/2}$) photoionization in xenon the five (and three) independent parameters of photoionization, i.e. the matrix elements and their relative phases. This approach was then applied very successfully to many other systems (Heinzmann and Cherepkov 1996, Snell *et al* 1997). However, different methods are being searched for to avoid the difficulties of the spin-polarization measurements and to replace these by some other technique, although these alternative approaches require specific properties of the system under study, i.e. they are not as general as a measurement of the spin-polarization parameters. One group of such complementary methods are experiments with polarized targets which can be prepared by laser excitation (Klar and Kleinpoppen 1982, Siegel *et al* 1983, Kerling *et al* 1990, Pahler *et al* 1992, Baier *et al* 1994, Wedowski *et al* 1995, von dem Borne *et al* 1997, Godehusen *et al* 1998) or by magnetic interaction of the atoms in a hexapole magnet (Plotzke *et al* 1996, Prümper *et al* 1997). Another group of complementary experiments is based on the information transfer from the photoionization process to a subsequent non-radiative or radiative decay process via the polarization (orientation, alignment) of the photoionized state. Here supplementary information to the common photoionization observables, cross section and angular distribution parameter, is provided by the coincident observation of the photoelectron with the emitted Auger electron (Kämmerling and Schmidt 1991, 1993, Kabachnik 1992, Schaphorst *et al* 1997) or with the emitted fluorescence light (Beyer *et al* 1995, Kabachnik and Ueda 1995, West *et al* 1996, 1998); in simple cases it is even sufficient to incorporate non-coincident data from the subsequent decay step (Kronast *et al* 1984, Jimenez-Mier *et al* 1986, Hausmann *et al* 1988, Becker 1990, Ueda *et al* 1993).

The present study belongs to the group in which photoionization data and non-coincident data from a subsequent Auger decay are used to extract the desired matrix elements for 3p photoionization in atomic calcium. Within the dipole approximation and Russell–Saunders coupling this photoionization process depends on two amplitudes and one relative phase only. These amplitudes will be abbreviated here by $R_{\epsilon\mathrm{d}}$ and $R_{\epsilon\mathrm{s}}$, because in the limit of independent particles they can be identified with the photoionization channels $3\mathrm{p} \to \epsilon\mathrm{d}$ for $R_{\epsilon\mathrm{d}}$ and $3\mathrm{p} \to \epsilon\mathrm{s}$ for $R_{\epsilon\mathrm{s}}$, where $R_{\epsilon\mathrm{d}}$ and $R_{\epsilon\mathrm{s}}$ are the radial integrals of the photoionization process which reduce in this limit to $R_{\epsilon\ell} = \int P_{\epsilon\ell}(r)\, r\, P_{3\mathrm{p}}(r)\, \mathrm{d}r$. For a complete experiment one therefore needs three independent photoionization observables to determine the magnitudes $|R_{\epsilon\mathrm{d}}|$ and $|R_{\epsilon\mathrm{s}}|$ and their relative phase $\Delta = \Delta_{\epsilon\mathrm{d}} - \Delta_{\epsilon\mathrm{s}}$, i.e. one has a three-parameter model for the photoionization process. In the present case photoionization occurs in an outer shell orbital of a low-Z element. Therefore, Russell–Saunders coupling is well fulfilled and the three-parameter model is valid to a good approximation. Beyond that, in a recent analysis by Becker and Langer (1998), it has been shown that the available complete experiments give strong evidence that such a three-parameter model has a more general validity than originally expected.

In analogy to the related case of 2p photoionization in magnesium (Hausmann *et al* 1988) complete information on the 3p process in calcium can be obtained by measuring: (a) the partial cross section $\sigma(3\mathrm{p})$; (b) the angular distribution parameter $\beta(3\mathrm{p})$ of the photoelectrons; and (c) the alignment parameter $\mathcal{A}_{20}(3\mathrm{p})$ of the photoion which can be obtained from the angular distribution parameter β_A of the subsequent Auger decay (M_3–$\mathrm{N}_1\mathrm{N}_1$). In contrast to the previous magnesium study, the related process in calcium finds more profound interest for two reasons. First, all ionization processes in calcium are subject to strong many-electron effects (electron correlations), because the 3d orbital which is not bound in the ground state of calcium is an important candidate for configuration interactions (one way to describe electron correlations) due to the possibility of a wavefunction collapse for increasing nuclear charge following 3p inner-shell ionization. Thus, 3p and 2p photoionization studies in calcium can be considered to be one of the ultimate objects for the study of many-electron effects (Wendin 1981). Secondly, within the independent-particle approximation the energy-dependent $R_{\epsilon\mathrm{d}}$ amplitude has a negative value at threshold and crosses zero at a certain photon energy value, i.e. there is a 'Cooper' minimum in the partial cross section. For such a case no complete experiment has been performed so far, and high-quality data are needed to prove whether the three-parameter model still applies in the presence of a Cooper minimum, or not, as supposed by Becker and Langer (1998). These two points make the experimental determination of matrix elements and relative phases for 3p photoionization in calcium within a broad energy range around the Cooper minimum a particular test case for a critical comparison between experimental and theoretical data.

For the present study the efforts of different groups have been combined. Since much information on 3p photoionization in calcium can be found in our previous publications (Deshmukh and Johnson 1983, Bizau *et al* 1987, Kämmerling *et al* 1994) we concentrate only on the aspects needed for the extraction of 3p photoionization matrix elements and relative phases. In particular, we refer to our previous work for experimental and theoretical details. This paper consists of three main parts. (a) The presentation of experimental data for the partial cross section σ(3p), the angular distribution parameter β(3p) of the photoelectrons and the alignment parameter $\mathcal{A}_{20}$(3p) of the photoion, measured via the angular distribution parameter $\beta_A(M_3–N_1N_1)$ of the Auger electrons; (b) the extraction of the amplitudes $R_{\epsilon d}$ and $R_{\epsilon s}$ and their relative phase Δ; and (c) the comparison of the latter with theoretical values obtained in the relativistic random-phase approximation (RRPA).

2. Experimental observables

In order to measure the three selected observables σ, β and $\mathcal{A}_{20}$ (via β_A) we used electron spectrometry. For the determination of σ we selected a magic-angle position of the electron spectrometer, while for the determination of β and β_A we performed angle-dependent measurements. The experiments were carried out at the electron storage rings BESSY in Berlin and Super ACO in Orsay.

Out of the three observables the cross section σ(3p) is the most difficult to assess, because one needs the absolute value of the partial cross section of the 3p main photoline, excluding

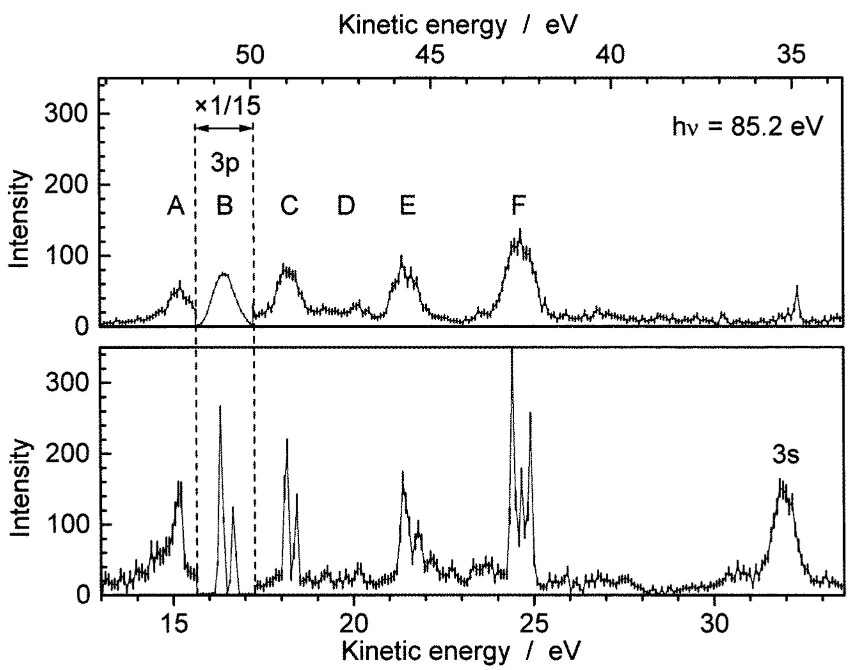

Figure 1. Spectrum of electrons ejected from atomic calcium by 85.2 eV photons, shown in two parts with different directions of the kinetic energy scale. Upper part, 3p photoline (intensity scaled down by a factor 15), called 'B', and discrete satellites 'A', 'C' to 'F'; the small structure at approximately 35 eV is due to the $L_{2,3}–M_1M_1$ Auger line in magnesium (small impurity in the calcium sample); the 4s photoline at 79.1 eV is outside the energy range shown here. Lower part, Auger decay of the 3p photoline with its corresponding discrete satellites, in addition, continuous photo-satellites; at 32.0 eV one can see the 3s main photoline (satellites at lower kinetic energy), and at 27.5 eV the 2p photoline of the magnesium impurity. The spectrum is free of background and it has been corrected for the energy dispersion of the electron analyser; the intensity given for the 3s photoline corresponds to the actual counting rate measured there in 6 s/channel.

Table 1. Compilation of partial photoionization cross sections of atomic calcium at 85 eV photon energy obtained from the electron spectrum of figure 1 (including the dispersion correction of the electrostatic analyser). Our relative intensities have been normalized to the total absorption cross section value $\sigma_{abs} = 1.24$ Mb taken from the compilation of Henke *et al* (1993) (no error bar can be given to this value). The contribution of discrete ('discr.') and continuous ('cont.') satellites ('sat.') is indicated.

	Relative intensities	Cross sections (Mb)
4s main	3.9 ± 0.1	0.025 ± 0.001
4s discr. + cont. sat.	0.4 ± 1.0	0.002 ± 0.006
4s main + sat.	4.3 ± 1.0	0.027 ± 0.006
3p main	100.0 ± 1.0	0.64 ± 0.02
3p discr. sat.	48.0 ± 2.0	0.31 ± 0.01
3p cont. sat.	8.0 ± 4.0	0.05 ± 0.03
3p main + sat.	156.0 ± 5.0	1.00 ± 0.04
3s main	16.2 ± 0.4	0.103 ± 0.004
3s discr. + cont. sat.	17.8 ± 2.0	0.11 ± 0.01
3s main + sat.	34.0 ± 2.0	0.21 ± 0.01
Sum	194 ± 5	1.24

satellite processes. In order to obtain the desired $\sigma(3p)$ cross section at particular photon energies we followed a three-step procedure. First, at the photon energy of 85 eV we have measured a complete spectrum of ejected electrons; the essential parts are shown in figure 1. The spectrum contains all energetically allowed photoprocesses, i.e. 4s, 3p and 3s main photolines and their discrete and continuous satellites (in the upper part of the figure), as well as subsequent Auger decays (in the lower part) if these are possible. By careful analysis of this spectrum the photoionization and Auger decay processes are identified and relative intensities of all photoprocesses are extracted. This yields the relative partial cross sections for main lines, $\sigma(n\ell)$, and satellite processes, $\sigma(n\ell, \text{sat.})$, collected under 'relative intensities' in table 1. In a next step the relation $\sigma_{abs} = \sigma(4s) + \sigma(4s, \text{sat.}) + \sigma(3p) + \sigma(3p, \text{sat.}) + \sigma(3s) + \sigma(3s, \text{sat.})$ is used together with a known value of the total absorption cross section σ_{abs} to place the relative partial cross sections on an absolute scale. However, accurate data of absolute absorption cross sections are difficult to obtain. Values recommended by Henke *et al* (1993) are based on both experimental data, mostly measured for solids, and theoretical calculations as well as interpolations across Z for the many elements where few measurements are available. If the photon energy is higher than 50 eV, these data can be transferred to free atoms outside of the resonance and absorption threshold regions. Since these conditions are fulfilled for our photon energy of 85 eV, we used the recommended data for atomic calcium and obtain for our photon energy the interpolated value $\sigma_{abs}(85 \text{ eV}) = 1.24$ Mb. It is difficult, however, to ascribe a realistic uncertainty to this value. Still, with this normalization we obtain the absolute partial cross sections listed under 'cross sections' in table 1. In a third step we determine the partial cross section values of 3p photoionization in calcium at other photon energies in a series of experiments where we measure at the magic angle the 3p main photoline of calcium simultaneously with the 1s main photoline of helium used to monitor the relative variation of the incident photon flux (avoiding energy regions where helium and calcium lines overlap). For constant target pressures the intensity ratio R of these photolines is then proportional to the corresponding cross section ratio. Hence, with known data for $\sigma(\text{He}, 1s)$ (Bizau and Wuilleumier 1995, adapted for the σ^{++}/σ^{+} ratio of Koßmann *et al* 1988, Koßmann 1992) the $\sigma(\text{Ca}, 3p)$ values can be calculated for each R. The results are shown in table 2, together with

Table 2. Compilation of experimental data of 3p photoionization in calcium (main line), partial cross section σ(3p), angular distribution parameter β(3p) of the photoelectrons and angular distribution parameter $\beta_A(M_3\text{–}N_1N_1)$ of Auger electrons.

Photon energy	σ(3p) (Mb)			
(eV)	From b	This work	β(3p)	$\beta_A(M_3\text{–}N_1N_1)$[a]
45.1	5.9 ± 0.9[c]	2.54 ± 0.14	1.87 ± 0.03	0.23 ± 0.03
54.0	0.96 ± 0.04	0.57 ± 0.04	1.28 ± 0.03	0.67 ± 0.05[c]
61.5	0.54 ± 0.08[c]	0.35 ± 0.03	-0.25 ± 0.03	0.92 ± 0.03
67.4	0.68 ± 0.10[c]	0.39 ± 0.02	-0.22 ± 0.02	0.75 ± 0.05
72.0	0.76 ± 0.11	0.48 ± 0.04	0.22 ± 0.03	0.54 ± 0.04
85.0	0.92 ± 0.14[c]	0.64 ± 0.02[d]	0.77 ± 0.03	0.38 ± 0.02
95.0	1.01 ± 0.15[c]	0.69 ± 0.03	1.00 ± 0.04	0.30 ± 0.02

[a] Data are from Kämmerling *et al* (1994), these authors also give measured values for $\beta_A(M_2\text{–}N_1N_1)$ which are zero within experimental uncertainties.
[b] Data are from Bizau *et al* (1987).
[c] Interpolated value from neighbouring photon energies.
[d] Normalization to σ_{abs} as described in the text.

Table 3. Compilation of partial cross section data for photoionization in calcium at 85 eV photon energy.

	Experiment[a] (Mb)	RRPA[b] (Mb)	LDRPA[c] (Mb)
4s process	0.03 ± 0.01	0.028	0.043
3p process	1.00 ± 0.04	1.181	1.184
3s process	0.21 ± 0.01	0.209	0.362
σ(total)	1.24	1.42	1.59

[a] Sum of experimental values for the $n\ell$ main line and its satellite contributions, adapted to yield the absorption cross section σ(total) from the compilation of Henke *et al* (1993).
[b] This work, theoretical ionization threshold adapted to the experimental value.
[c] From Bizau *et al* (1987).

the independently measured angular distribution parameters $\beta(\mathrm{Ca}, 3\mathrm{p})$ and $\beta_A(\mathrm{Ca}, M_3\text{–}N_1N_1)$. Finally, in table 3 we give a compilation of partial cross section data at 85 eV photon energy.

3. Extraction of matrix elements and their relative phase

The extraction of the matrix elements and their relative phases from a set of experimental data is based on relations which show explicitly how these quantities enter the observables (cf the compilation in Schmidt 1992). As pointed out in the introduction these relations depend on the application of a certain model, here the dipole approximation and Russell–Saunders coupling (LS-coupling limit). Within the dipole approximation one has the general photoionization amplitudes D_+, D_0, D_- for $3\mathrm{p}_{3/2}$ photoionization and $\tilde{D}_+$, $\tilde{D}_0$ for $3\mathrm{p}_{1/2}$ photoionization (see Huang 1980). For $D_j = |D_j| \exp(\mathrm{i}\Delta_j)$ these are given in the LS-limit by (see Schmidt 1992)

$$\begin{aligned} |D_+| &= \frac{6}{\sqrt{15}}|R_{\epsilon\mathrm{d}}| \qquad |D_0| = \frac{2}{\sqrt{15}}|R_{\epsilon\mathrm{d}}| \qquad |D_-| = \frac{2}{\sqrt{3}}|R_{\epsilon\mathrm{s}}| \\ |\tilde{D}_+| &= \frac{2}{\sqrt{3}}|R_{\epsilon\mathrm{d}}| \qquad |\tilde{D}_0| = \sqrt{\frac{2}{3}}|R_{\epsilon\mathrm{s}}| \end{aligned} \tag{1a}$$

and

$$\begin{aligned} &\Delta_{+} = \Delta_{\epsilon \mathrm{d}} \qquad \Delta_0 = \Delta_{\epsilon \mathrm{d}} \qquad \Delta_{-} = \Delta_{\epsilon \mathrm{s}} \\ &\tilde{\Delta}_{+} = \Delta_{\epsilon \mathrm{d}} \qquad \tilde{\Delta}_0 = \Delta_{\epsilon \mathrm{s}} + \pi \end{aligned} \tag{1b}$$

where $R_{\epsilon \mathrm{d}}$, $R_{\epsilon \mathrm{s}}$, $\Delta_{\epsilon \mathrm{d}}$ and $\Delta_{\epsilon \mathrm{s}}$ have been introduced above. An alternative way to describe this photoionization process is the angular momentum transfer approach (Fano and Dill 1972, Dill and Fano 1972). There the LS-coupling limit corresponds to a vanishing of the parity unfavoured scattering amplitude $S_2(2)$. Thus, one has $S_2(2) = 3D_0 - D_+$ (cf Becker 1990).

Describing 3p photoionization in calcium by the amplitudes $|R_{\epsilon \mathrm{d}}|$ and $|R_{\epsilon \mathrm{s}}|$ and their relative phase Δ, one obtains for the present case (cf the compilation in Schmidt 1992), using atomic units and the length form of the dipole matrix elements:
for the partial cross section

$$\sigma(3\mathrm{p}) = \tfrac{8}{3}\pi^2 \alpha \omega (|R_{\epsilon \mathrm{s}}|^2 + 2|R_{\epsilon \mathrm{d}}|^2) \tag{2}$$

for the angular distribution parameter of the photoelectrons

$$\beta(3\mathrm{p}) = \frac{2|R_{\epsilon \mathrm{d}}|^2 - 4|R_{\epsilon \mathrm{s}}||R_{\epsilon \mathrm{d}}| \cos \Delta}{|R_{\epsilon \mathrm{s}}|^2 + 2|R_{\epsilon \mathrm{d}}|^2} \tag{3}$$

where α is the fine-structure constant and ω is the photon energy. For the angular distribution parameter of the two fine-structure components of the subsequent Auger transition one obtains (the alignment parameter $\mathcal{A}_{20}(^2\mathrm{P}_{3/2})$ is defined for the quantization axis pointing into the direction of the electric field vector of linearly polarized incident light, cf Schmidt (1992)):

$$\begin{aligned} &\beta_{\mathrm{A}}(\mathrm{M}_2\text{–}\mathrm{N}_1\mathrm{N}_1) = 0 \\ &\beta_{\mathrm{A}}(\mathrm{M}_3\text{–}\mathrm{N}_1\mathrm{N}_1) = \frac{|R_{\epsilon \mathrm{s}}|^2 + \frac{1}{5}|R_{\epsilon \mathrm{d}}|^2}{|R_{\epsilon \mathrm{s}}|^2 + 2|R_{\epsilon \mathrm{d}}|^2} = -\mathcal{A}_{20}(^2\mathrm{P}_{3/2}). \end{aligned} \tag{4}$$

Using these expressions, the amplitudes $|R_{\epsilon \mathrm{d}}|$ and $|R_{\epsilon \mathrm{s}}|$ and their relative phase Δ can be derived from the experimental data. The results are shown in table 4. Several comments are necessary. Firstly, it is only the absolute value of $\sigma(3\mathrm{p})$ which fixes, and in turn is fixed by, the actual magnitudes of $|R_{\epsilon \mathrm{d}}|$ and $|R_{\epsilon \mathrm{s}}|$. In contrast, the angular distribution parameters depend on the ratio $|R_{\epsilon \mathrm{d}}|/|R_{\epsilon \mathrm{s}}|$ where some cancellation in the magnitudes of $|R_{\epsilon \mathrm{d}}|$ and $|R_{\epsilon \mathrm{s}}|$ can occur. Only the β(3p) parameter provides information on the relative phase Δ. Secondly, because of $\cos(2\pi \pm \Delta) = \cos \Delta$ there are two solutions for Δ, e.g. $\Delta_{\mathrm{exp},1}(85\ \mathrm{eV}) = 1.63$ rad and

Table 4. Compilation of experimental $R_{\epsilon \mathrm{d}}$ and $R_{\epsilon \mathrm{s}}$ amplitudes and their relative phase Δ for 3p photoionization in calcium.

Photon energy (eV)	Kinetic energy (eV)	$\|R_{\epsilon \mathrm{s}}\|$ (au)	$\|R_{\epsilon \mathrm{d}}\|$ (au)	$R_{\epsilon \mathrm{d}}^{\mathrm{mod}}$ (au)	Δ (rad)[a]	Δ^{mod} (rad)
45.1	10.7	0.21 ± 0.02[b]	0.35 ± 0.01[b]	-0.35 ± 0.01[b,c]	3.14 ± 0.30[b]	0.00 ± 0.30[b]
54.0	19.6	0.18 ± 0.01	0.10 ± 0.01	-0.10 ± 0.01[c]	3.97 ± 0.09	0.83 ± 0.09
61.5	27.1	0.161 ± 0.007	0.037 ± 0.006	0.037 ± 0.006	1.14 ± 0.05	1.14 ± 0.05
67.4	33.0	0.145 ± 0.007	0.064 ± 0.007	0.064 ± 0.007	1.16 ± 0.03	1.16 ± 0.03
72.0	37.6	0.128 ± 0.008	0.093 ± 0.006	0.093 ± 0.006	1.36 ± 0.04	1.36 ± 0.04
85.0	50.6	0.108 ± 0.004	0.115 ± 0.003	0.115 ± 0.003	1.63 ± 0.03	1.63 ± 0.03
95.0	60.6	0.089 ± 0.005	0.120 ± 0.003	0.120 ± 0.003	1.76 ± 0.04	1.76 ± 0.04

[a] Obtained from equations (3) and (4) by using the ratio $|R_{\epsilon \mathrm{d}}|/|R_{\epsilon \mathrm{s}}|$ which has smaller error bars than the individual $R_{\epsilon \mathrm{d}}$ and $R_{\epsilon \mathrm{s}}$ values.
[b] Values follow from a χ^2-fit based on $R_{\epsilon \mathrm{d}}/R_{\epsilon \mathrm{s}}$ and Δ to β(3p) and $\beta_{\mathrm{A}}(\mathrm{M}_3\text{–}\mathrm{N}_1\mathrm{N}_1)$.
[c] The minus sign for $R_{\epsilon \mathrm{d}}^{\mathrm{mod}}$ has been taken from the phase Δ by changing the latter to Δ^{mod} in order to obtain a smooth crossing through the Cooper minimum.

$\Delta_{\mathrm{exp},2}(85\ \mathrm{eV}) = 4.65$ rad. This ambiguity can be solved if an additional observable (which depends on $\sin\Delta$) is taken into account, such as for example the spin-polarization parameter η (see relations in Huang *et al* 1981), or if the single-particle description is used following guidance from theoretical calculations. To give an example for the latter case, we selected a photon energy of 85 eV and obtain $\Delta(85\ \mathrm{eV}) \approx 1.6$ rad. Here we have calculated the difference of Coulomb phases from $\Delta_{\mathrm{C}} = -\tan^{-1}(1/\sqrt{2\epsilon}) - \tan^{-1}(1/(2\sqrt{2\epsilon}))$, where ϵ is the kinetic energy of the photoelectron in atomic units, and we took the differences introduced by the short-range potential from an extrapolation of the data given by Manson (1969). The value obtained is also in accord with the phase difference calculated in RRPA. Thus, we select the first solution, $\Delta_{\mathrm{exp},1}$. Third, the magnitude of $|R_{\epsilon\mathrm{d}}|$ cannot be negative by definition, but zero is allowed. As will be seen below (figure 2) the $|R_{\epsilon\mathrm{d}}|$ values show a minimum close to zero at about 59.0 eV photon energy which defines the position of the Cooper minimum. Hence, it is illustrative to assume a zero-crossing of a real amplitude $R_{\epsilon\mathrm{d}}^{\mathrm{mod}}$ which starts at lower photon energies with a negative value, as given in the single-particle model. Therefore, we introduce for photon energies below 59.0 eV the additional parameters $R_{\epsilon\mathrm{d}}^{\mathrm{mod}} = -|R_{\epsilon\mathrm{d}}|$ and $\Delta^{\mathrm{mod}} = \Delta - \pi$ (see table 4).

4. Comparison of experimental and theoretical data

Traditionally a comparison of experimental and theoretical data concentrates directly on selected observables. However, from a complete experimental study a deeper and more general insight can be obtained if the transition matrix elements (including their phase differences) are compared directly. This aspect has been discussed exemplarily for 2p photoionization in magnesium at the particular photon energy of 80 eV (Schmidt 1997, p 207). Here we will concentrate on the energy dependences of the photoionization amplitudes $|R_{\epsilon\mathrm{d}}|$ and $|R_{\epsilon\mathrm{s}}|$ and their relative phase Δ in the region around the Cooper minimum, comparing experimental and theoretical data. Since we are going to compare absolute values of the two matrix elements and since these are fixed by the absolute magnitude of $\sigma(3\mathrm{p})$, this partial cross section shall be discussed first.

The $\sigma(3\mathrm{p})$ values in table 2 come from individual measurements and they are subject to an overall scaling factor which relies on the normalization of $\sigma(3\mathrm{p}, 85\ \mathrm{eV})$ to $\sigma_{\mathrm{abs}}(85\ \mathrm{eV})$. In comparison to the former results of Bizau *et al* (1987) one notes that the present cross section values are considerably smaller (compare columns 2 and 3 in table 2), which indicates different scaling factors, and further that no constant ratio exists between both data sets which indicates different photon-energy-dependent normalizations. We consider the present data to be more accurate for the following reasons. Bizau *et al* have added to the intensity of their 3p photoline a constant satellite contribution of 25% and then they normalized it to the theoretical 3p photoionization cross section calculated in the LDRPA. In the present work we find for this satellite intensity at 85 eV photon energy about twice this value. The origin of this difference can be attributed to problems in the background subtraction in the earlier spectra obtained with a lower resolution. Further, different approaches were applied to obtain the energy-dependent photon intensity. In the previous experiment the photocurrent from a gold mesh was used as a reference, while in the present experiment the intensity of the simultaneously measured 1s photoline of helium monitors the relative variation of the photon flux. With known $\sigma(1\mathrm{s})$ data of helium the last method allows more accurate determination of relative photon intensities, to be obtained independently of the actual gold yield and higher-order contributions in the monochromatized light.

As demonstrated in table 3, our $(\sigma(4\mathrm{s}) + \sigma(4\mathrm{s}, \mathrm{sat.}))$, $(\sigma(3\mathrm{p}) + \sigma(3\mathrm{p}, \mathrm{sat.}))$ and $(\sigma(3\mathrm{s}) + \sigma(3\mathrm{s}, \mathrm{sat.}))$ values at 85 eV photon energy are in close agreement with the RRPA results (against in the LDRPA calculations, there exist significant differences for the 2s and 3s cross sections). Taking into account the remarkable contribution of satellite intensities, this finding confirms the intensity-borrowing model in which the satellites ‘borrow’ their intensity from the process calculated in these mean-field approximations. The direct calculation of photoionization processes for main lines and satellites is beyond RRPA and LDRPA, because, in addition to the mean-field effects of the electron–electron interaction, one ought to include explicitly in the theory the correlated motion of the electrons. A calculation into this direction has been reported by Walter and Schirmer (1981): within the two-particle-hole Tamm–Dancoff approximation and in the limit of large photon energy, they obtain that for 4s, 3p and 3s photoionization in calcium 7%, 18% and 35% of the single-particle oscillator strength is transferred to satellite intensities. Comparison with our results in table 1 shows that the theoretical data for 3s and 3p still underestimate the actual situation.

Before experimental and theoretical data for the matrix elements and their relative phase can be compared, the RRPA results obtained for $3p_{3/2}$ and $3p_{1/2}$ photoionization must be converted to obtain the corresponding nonrelativistic LS-coupling limit. For this purpose we use the relations in equation (1), derive individual $|R_{\epsilon d}|$, $|R_{\epsilon s}|$ and Δ values and take the average of them. The two requirements of the LS-coupling limit are well fulfilled: the ratio $D_0(3p_{3/2})/D_+(3p_{3/2}) = \frac{1}{3}$ holds within less than 1% for photon energies which are more than

Table 5. Compilation of theoretical $R_{\epsilon d}$ and $R_{\epsilon s}$ amplitudes and their relative phase Δ for 3p photoionization in calcium. The numbers in parentheses describe the maximum deviations between the average values and the individual RRPA data transformed to the LS-coupling limit; if no number is given the error is smaller than the last digit. Note that all phases given here are subject to modulo (2π).

Photon energy (eV)	Kinetic energy (eV)	$\lvert R_{\epsilon s}\rvert$ (au)	$\lvert R_{\epsilon d}\rvert$ (au)	$R_{\epsilon d}^{\mathrm{mod}}$ (au)	Δ (rad)	Δ^{mod} (rad)
40.0	5.6	0.378(4)	0.919(16)	−0.919(16)	−3.877(33)	−0.736(33)
45.0	10.6	0.302(3)	0.498(14)	−0.498(14)	−3.139(10)	0.003(10)
45.1	10.7	0.301(3)	0.491(14)	−0.491(14)	−3.128(10)	0.014(10)
50.0	15.6	0.265(3)	0.238(11)	−0.238(11)	−2.663(10)	0.479(10)
54.0	19.6	0.244(2)	0.109(10)	−0.109(10)	−2.380(14)	0.761(14)
55.0	20.6	0.239(2)	0.084(10)	−0.084(10)	−2.315(16)	0.827(16)
61.5	27.1	0.214(1)	0.035(7)	0.035(7)	1.026(48)	1.026(48)
65.0	30.6	0.202(1)	0.073(6)	0.073(6)	1.176(15)	1.176(15)
67.4	33.0	0.194(1)	0.094(5)	0.094(5)	1.251(11)	1.251(11)
70.0	35.6	0.186(1)	0.111(5)	0.111(5)	1.321(8)	1.321(8)
72.0	37.6	0.180(1)	0.122(4)	0.122(4)	1.370(7)	1.370(7)
75.0	40.6	0.171(1)	0.134(4)	0.134(4)	1.436(6)	1.436(6)
80.0	45.6	0.158	0.148(3)	0.148(3)	1.533(5)	1.533(5)
85.0	50.6	0.147	0.156(3)	0.156(3)	1.617(5)	1.617(5)
90.0	55.6	0.136	0.160(2)	0.160(2)	1.690(5)	1.690(5)
95.0	60.6	0.127	0.161(2)	0.161(2)	1.754(4)	1.754(4)
100.0	65.6	0.118	0.160(2)	0.160(2)	1.812(4)	1.812(4)
110.0	75.6	0.103	0.153(1)	0.153(1)	1.912(4)	1.912(4)
120.0	85.6	0.091	0.146(1)	0.146(1)	1.998(4)	1.998(4)
130.0	95.6	0.081	0.137(1)	0.137(1)	2.075(4)	2.075(4)
140.0	105.6	0.072	0.129(1)	0.129(1)	2.143(4)	2.143(4)
150.0	115.6	0.065	0.121	0.121	2.205(3)	2.205(3)
160.0	125.6	0.058	0.113	0.113	2.260(3)	2.260(3)
170.0	135.6	0.053	0.106	0.106	2.311(3)	2.311(3)
180.0	145.6	0.048	0.099	0.099	2.358(3)	2.358(3)

± 15 eV away from the Cooper minimum (note that each of these amplitudes is close to zero at the Cooper minimum); the phase difference $\Delta_0(3p_{3/2}) - \Delta_+(3p_{3/2}) = 0$ holds within less than 1% for all photon energies which are more than ± 3 eV away from the Cooper minimum. In addition, the individual $|R_{\epsilon d}|$, $|R_{\epsilon s}|$ and Δ values for $3p_{3/2}$ and $3p_{1/2}$ photoionization agree within the same level of accuracy (see table 5). This demonstrates that relativistic effects in the 3p photoionization of calcium are negligibly small and the three-parameter model applies very well.

The theoretical RRPA results are given originally on a photon energy scale and refer to Dirac–Fock ionization energies $E_I(3p_{3/2}) = 36.29$ eV and $E_I(3p_{1/2}) = 36.71$ eV. The statistically weighted average of these ionization energies is $E_I(3p, \text{theor.}) = 36.43$ eV which

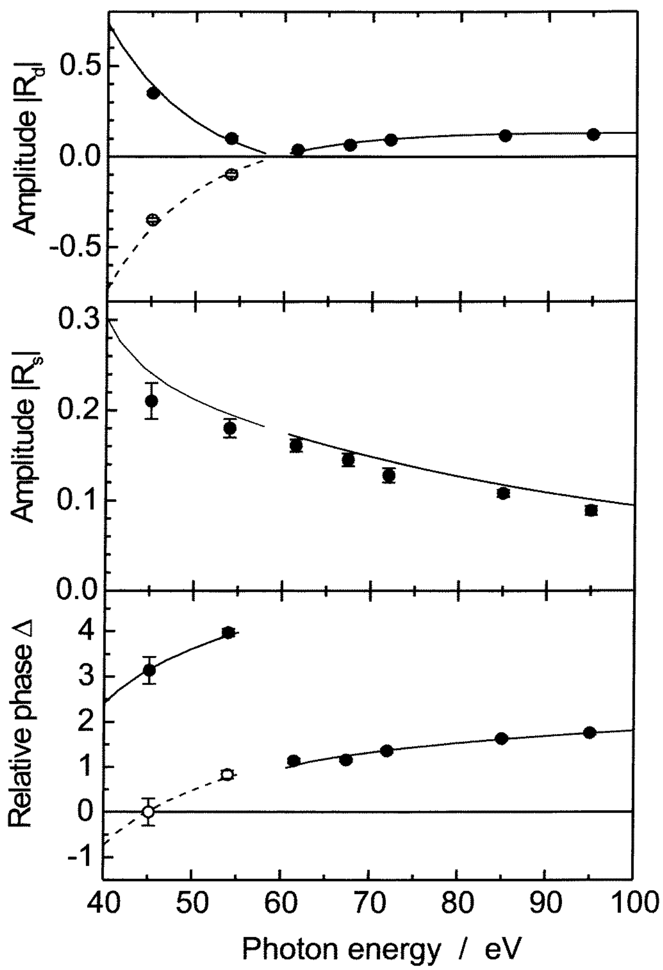

Figure 2. Graphical representation of dipole amplitudes $R_{\epsilon d}$ and $R_{\epsilon s}$ and their relative phase Δ for 3p photoionization in atomic calcium in the region around the Cooper minimum at 59.0 eV photon energy. Top, $|R_{\epsilon d}|$ (——, ●) and $R_{\epsilon d}^{\text{mod}}$ (– – –, ○); middle, $|R_{\epsilon s}|$ (——, ●); bottom, Δ (——, ●) and Δ^{mod} (– – –, ○), as a function of photon energy. Experimental data: points with error bars; RRPA results transferred to the LS-coupling limit as described in the main text: full and broken curves; the $R_{\epsilon d}$ and $R_{\epsilon s}$ amplitudes of the calculation have been multiplied with the factor 0.8 in order to take into account satellite processes as observed experimentally at 85 eV photon energy.

differs significantly from the experimental value $E_{\mathrm{I}}(3\mathrm{p}, \mathrm{expt}) = 34.43$ eV. The difference can be ascribed to a self-energy correction caused by electron correlations which is missing in the RRPA calculation. However, to a first approximation these correlation effects can be taken into account if the theoretical binding energy is replaced by the experimental value (this shifts the theoretical data as a whole; note that this approach completely fails if the subsequent decay process is so important that it affects the primary process, such as in 4p photoionization in xenon, Wendin and Ohno 1976). Applying the self-energy correction, we take the average $|R_{\epsilon\mathrm{d}}|$, $|R_{\epsilon\mathrm{s}}|$ and Δ values obtained from theory at $E_{\mathrm{kin}}(3\mathrm{p}) = h\nu^{\mathrm{th}} - 36.43$ eV and adapt them to the kinetic energy values $E_{\mathrm{kin}}(3\mathrm{p}) = h\nu - 34.43$ eV; i.e. we apply a shift $h\nu^{\mathrm{th}} = h\nu + 2.00$ eV. The results are collected in table 5.

In figure 2 we show our experimental results for the calcium 3p photoionization amplitudes $|R_{\epsilon\mathrm{d}}|$ and $|R_{\epsilon\mathrm{s}}|$ and their relative phase Δ, and compare these data with the theoretical RRPA results. The theoretical data for $|R_{\epsilon\mathrm{d}}|$ and $|R_{\epsilon\mathrm{s}}|$ have been multiplied by a factor of 0.8. Within the intensity-borrowing model the squared value of this factor is the ratio of the 3p main-line intensity to the 3p main and satellite intensity (cf Kämmerling *et al* 1994). At 85 eV photon energy we measured for this ratio the value 0.64 (see table 1). From figure 2 it can be seen that in the whole energy range around the Cooper minimum there is excellent agreement between the scaled theoretical RRPA results and the experimental data. Also, one can nicely follow the 'zero' crossing of the $R_{\epsilon\mathrm{d}}^{\mathrm{mod}}$ amplitude at approximately 59.0 eV photon energy. Concerning the magnitude of $|R_{\epsilon\mathrm{d}}|$ and $|R_{\epsilon\mathrm{s}}|$ such good agreement was not expected because the presence of the Cooper minimum with the disappearance of one photoionization channel is a rather sensitive indicator of electron correlations which can have a different influence on the ϵd and ϵs ionization channels. Therefore, neglecting the small systematic deviation between experimental and theoretical $|R_{\epsilon\mathrm{s}}|$ values, our data demonstrate two important results: firstly, both photoionization channels have the same strength for intensity borrowing and secondly, this intensity borrowing is constant over the whole range of photon energies, including the critical region around the Cooper minimum.

5. Conclusion

The most sophisticated complete photoionization experiment, i.e. spin- and angle-resolved photoelectron spectroscopy, has to face two major difficulties: low detection efficiency and the availability of circularly polarized light over broad energy ranges, which is very scarce at all second generation synchrotron radiation laboratories, but will become more commonly available with third generation sources. In the present work we have shown that the difficulties of the spin-polarization measurements can be overcome for suitably selected systems by alternative experiments, here the measurements of non-coincident data for photoionization and a subsequent Auger decay. For 3p photoionization in atomic calcium we have been able for the first time to extract directly the two matrix elements and their relative phase. The high accuracy of our experimental data did allow an extensive comparison between experiment and theory in the photon energy range surrounding the Cooper minimum, which provides a particular sensitive case. We could demonstrate that the RRPA results which include interchannel couplings between the $4\mathrm{s}_{1/2}$, $3\mathrm{p}_{3/2}$, $3\mathrm{p}_{1/2}$ and $3\mathrm{s}_{1/2}$ ionization channels give in their non-relativistic LSJ-coupling limit an excellent description for the experimentally derived 3p photoionization matrix elements and their relative phase. Remarkably, this agreement holds for the absolute magnitude of these matrix elements if the considerable satellite intensity is taken into account by a constant and channel-independent spectroscopic factor. So our results clearly demonstrate the modification of the main photoprocess by satellite transitions and the applicability of the RRPA approximation for a quantitative analysis of the observed photoionization phenomena.

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