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Autoionization dynamics of even Ar ($3p_{1/2}^5 np'$, nf') resonances: Comparison of experiment and theory

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Abstract. The $3p_{1/2}^5 np'$ $J = 0, 1, 2$ and $3p_{1/2}^5 nf'$ $J = 2$ autoionizing Rydberg states (ARS) of Ar have been studied by two-step two-color photoionization of ground-state argon atoms via the intermediate levels $3p_{1/2}^5 4s'$ $[1/2]_1$, $3p_{3/2}^5 5s$ $[3/2]_1$ and $3p_{3/2}^5 3d$ $[1/2]_1$, followed by time-of-flight ion detection. Accurate energy positions and widths have been determined for the $15p'$ $[1/2]_0$, $15p'$ $[3/2]_2$ and $13f'$ $[5/2]_2$ resonances. The measured spectra and earlier results obtained for the intermediate levels $5s'$ $[1/2]_1$, $7s'$ $[1/2]_1$, and $8s$ $[3/2]_1$ are compared with absolute cross sections, calculated with the configuration interaction Pauli-Fock core-polarization (CIPFCP) method.

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1. Introduction.

The photoionization spectra of the rare gas atoms Rg = Ne, Ar, Kr and Xe between the two lowest ionization thresholds $mp_{3/2}^5$ and $mp_{1/2}^5$ ($m = 2 - 5$) are dominated by resonances corresponding to Rg $mp_{1/2}^5 n\ell'[K']_J$ autoionizing Rydberg states (ARS) which belong to series converging on the higher ionization threshold $Rg^+ mp_{1/2}^5$ and decay to $Rg^+ mp_{3/2}^5 \varepsilon\ell, J$ continuum states (Beutler 1935, Berkowitz 1979) (Rydberg states belonging to series converging to the $^2P_{1/2}$ threshold are marked with primed quantum numbers ℓ' and K' , where K' results from coupling the total angular momentum of the mp^5 core with the orbital angular momentum $\vec{\ell}'$ of the Rydberg electron). The autoionization process is mediated by the Coulomb interaction between the Rydberg electron and the core electrons. The linewidths, energy positions and shapes of the ARS are substantially influenced by electron correlation effects. Thus accurate measurements of these properties provide tests of advanced theoretical descriptions (see, e.g. (Johnson *et al* 1980, Klar *et al* 1992, Petrov *et al* 2003)).

Over the last few years, two-photon excitation studies of ground state Ne (Petrov *et al* 2006b) and Ar (Lee *et al* 2008) atoms via several short-lived intermediate, odd-parity $J = 1$ levels as well as one-photon excitation from the respective $mp^5(m+1)s, J = 2, 0$ metastable levels (Peters *et al* 2005, Petrov *et al* 2006a, Wright *et al* 2008) yielded new results on the lineshapes of the even-parity $np' J = 0, 1, 2$ and $nf' J = 2$ autoionizing Rydberg states (ARS) the proper description of which poses a substantial challenge to theory. Calculations of the shapes, widths and energy positions of the Ne(np') ARS by means of the configuration-interaction Pauli-Fock core-polarization (CIPFCP) method (see, e.g., (Peters *et al* 2005, Petrov *et al* 2006a, Petrov *et al* 2009)) were found to be in good overall agreement with experimental results (Petrov *et al* 2006b) only after proper inclusion of an interference effect between the direct $\langle 3s|\mathbf{r}|np \rangle$ and the intershell $\langle 3s|\mathbf{r}|3p \rangle \langle 3p|V(2p2p)|np \rangle$ amplitudes. This interference turned out to be constructive in the $3s' \rightarrow np'$ transitions and destructive in the $3s \rightarrow np'$ transitions. Spectra of Ar(np') ARS, excited from the $4s [3/2]_1$ and $4s'[1/2]_1$ levels, were computed to be similar (Petrov *et al* 2006a) to those observed for Ne(np') from the $3s [3/2]_1$ and $3s' [1/2]_1$ levels (Petrov *et al* 2006b) when the corresponding intershell amplitudes were taken into account, but no clear experimental results are available so far to confirm these predictions.

Stepwise two-photon excitation of Ar atoms with synchrotron and laser radiation has been used to access the np' and nf' ARS via seven odd-parity $J = 1$ intermediate levels, namely $3d'[3/2]_1$, $5d'[3/2]_1$, $5s'[1/2]_1$, $7s'[1/2]_1$, $6d[1/2]_1$, $6d[3/2]_1$, and $8s[3/2]_1$ (Lee *et al* 2008). The spectra excited via the nd and nd' levels were all found to be dominated by the nf' ARS. The background continuum was substantially stronger in the spectra excited from the nd levels which was attributed to the predominant $J_c = 3/2$ character of the $3p^5$ core for the nd levels. The np' spectra excited from the $5s'[1/2]_1$ and $8s[3/2]_1$ levels are similar in shape to that calculated for $4s'[1/2]_1$ while in the spectrum excited from the $7s'[1/2]_1$ level the $np' J = 0$ resonance is less intense and

shifted towards lower energies. Lee *et al* (2008) emphasized the substantial difference between the experimental spectrum recorded from $8s[3/2]_1$ (showing a strong peak for the $14p'$ $J = 0$ resonance) and that calculated by Petrov *et al* (2006a) for excitation from $4s[3/2]_1$ (in which the $np'[1/2]_0$ resonance appears as a weak minimum) and pointed out that a simpler calculation for $4s[3/2]_1$ which ignores the interference effect is superior to the more elaborate one because it yields a clear peak for the $J = 0$ resonance. To resolve this paradox additional calculations for several intermediate levels, including the $7s'[1/2]_1$ and $8s[3/2]_1$ states, must be carried out. Moreover, new experimental data, especially for the low-lying $ns[3/2]_1$ and $ns'[1/2]_1$ levels, which are not strongly mixed with each other, are needed to validate the calculations.

In this paper, we present highly-resolved spectra of the Ar(np' , nf') ARS (with n around 14), excited from the intermediate levels $4s'[1/2]_1$, $5s[3/2]_1$, and $3d[1/2]_1$, the latter being reached from the ground state of Ar by pulses of narrowband VUV radiation. For comparison with the experimental spectra, obtained following excitation from the intermediate levels $4s[3/2]_1$, $4s'[1/2]_1$, $5s[3/2]_1$, $5s'[1/2]_1$, $3d[1/2]_1$, $7s'[1/2]_1$, and $8s[3/2]_1$, we present absolute cross sections calculated with the CIPFCP method. The $7s'[1/2]_1$, and $8s[3/2]_1$ levels (energetic separation of only 6.6 meV) are strongly mixed by configuration interaction. When this interaction is taken into account the calculated spectra for these intermediate levels exhibit lineshapes in satisfactory agreement with the experimental data of Lee *et al* (2008). The np' ARS excited from $4s'[1/2]$ and $5s[3/2]$ are strongly influenced by the fact that the $J = 1$ and $J = 2$ amplitudes are near zero (i.e., are close to a Seaton-Cooper minimum). This paper is organized as follows. In section 2, we briefly describe the experimental procedure and setup. In section 3, we summarize the essential aspects of the theory. In section 4, we compare the calculated cross sections with the new experimental spectra and the spectra of Lee *et al* (2008). The article ends with a short conclusion in section 5.

2. Experimental procedure and set-up

2.1. Excitation scheme

As shown in figure 1a, five autoionizing Rydberg series, (i) the $np'[1/2]_0$, (ii) the $np'[1/2]_1$, (iii) the $np'[3/2]_1$, (iv) the $np'[3/2]_2$, and (v) the $nf'[5/2]_2$ series are accessible from the Ar($3p^6$ 1S_0) ground state following two-photon excitation via the $3d[1/2]_1$, $5s[3/2]_1$ and $4s'[1/2]_1$ intermediate levels.

In the present experiments, the two laser beams (see figure 1b) had linear polarizations and crossed in a perpendicular configuration. Previous resonant two-photon excitation work has shown that the excitation probability of states with different total angular momentum strongly depends on the choice of the two polarization directions (see, e.g., (Klar *et al* 1992)). When the polarization vectors of the two excitation laser beams are chosen to be orthogonal, the final states must have $M_J = \pm 1$ and the $J = 0$ series (i) is not accessible. When they are chosen to be parallel, excitation

Figure 1. a) Energy level diagram of Ar with the two-photon excitation scheme used in the experiment. b) The spatial arrangement of the gas beam, the laser beams and their polarization vectors: The skimmed supersonic beam of the sample gas (argon) propagates along the z axis and crosses at right angles the VUV beam ($\tilde{\nu}_{\text{VUV}}$) and the second excitation laser beam ($\tilde{\nu}_3$) that propagate along the x and the y axis, respectively. The crossing point is located on the axis (z axis) of the TOF mass spectrometer.

to the two $J = 1$ series (ii) and (iii) is forbidden because the $3j$ -symbol $\begin{pmatrix} 1 & 1 & 1 \\ 0 & 0 & 0 \end{pmatrix}$ which is included in the transition moments as an angular momentum factor is zero (e.g., (Zare 1988), see also equation (10) in (Petrov *et al* 2006b)). One thus expects three series ((i), (iv) and (v)) to contribute to the spectra recorded with a parallel arrangement of the polarization vectors, and four series ((ii), (iii), (iv) and (v)) to be observable for a perpendicular arrangement.

2.2. Experiment

As explained in section 2.1 (see also excitation scheme in figure 1a), the measurements relied on a resonance-enhanced ($1_{\text{VUV}} + 1'_{\text{UV/VIS}}$) two-photon excitation sequence via the 3d, 5s or 4s' intermediate level to excite the autoionizing nf' and np' Rydberg states just above the $^2P_{3/2}$ ionization threshold of argon. The VUV wavenumbers ($\tilde{\nu}_{\text{VUV}} = 2\tilde{\nu}_{\text{UV}} + \tilde{\nu}_2$) at 111 818.03 cm⁻¹, 114 975.02 cm⁻¹ and 95 399.83 cm⁻¹ which were used to drive the transitions from the 1S_0 ground state to the 3d, 5s and 4s' levels, respectively, were generated by resonance-enhanced sum-frequency mixing in a xenon gas jet. The four-wave mixing process was resonantly enhanced by fixing the doubled wavenumber $\tilde{\nu}_{\text{UV}}$ of the first laser at the position of the $5p^6 \rightarrow 5p^5 6p[1/2]_0$ two-photon transition of xenon ($2\tilde{\nu}_{\text{UV}} = 80\,118.962\text{ cm}^{-1}$), and the VUV wavenumber was adjusted to the positions of the 3d, 5s and 4s' resonances of argon by scanning the wavenumber $\tilde{\nu}_2$ of the second laser. The VUV beam was separated from the beams of wavenumbers $\tilde{\nu}_{\text{UV}}$ and $\tilde{\nu}_2$ and from beams of other frequencies generated by other nonlinear processes using a vacuum monochromator with a toroidal gold-coated grating and recollimated towards the excitation region. Photoionization spectra of argon excited from the intermediate levels 3d, 5s and 4s' to the autoionization region just above the $^2P_{3/2}$ ionization threshold were recorded by monitoring the Ar^+ ionization signal as a function of the wavenumber $\tilde{\nu}_3$ of the second excitation laser in the experimental configuration depicted schematically in figure 1b.

The excitation sequence required the use of three tunable lasers (see figure 2). The first one, a commercial Nd:YAG(355 nm)-pumped pulsed dye laser with a bandwidth of 0.04 cm⁻¹ in the fundamental, was frequency doubled in a β -barium-borate (BBO) crystal. The doubled wavenumber $\tilde{\nu}_{\text{UV}} = 2\tilde{\nu}_1$ was kept fixed in the experiments as explained above. The other two dye laser beams were generated by pulsed amplification of the single-mode outputs of continuous-wave ring dye lasers using amplification lines consisting each of three dye cells pumped transversally by the 532 nm output of the Nd:YAG laser. These two dye lasers had a near-Fourier-transform-limited bandwidth of ≈ 150 MHz in the fundamental (Hollenstein *et al* 2000). In experiments carried out through the 3d[1/2]₁ and 5s[3/2]₁ intermediate levels, the output of the first of these two narrow-band dye lasers ($\tilde{\nu}_2$) had to be frequency doubled in a BBO crystal while the fundamental output of the second ($\tilde{\nu}_3$) is used. In experiments carried out through the 4s'[1/2]₁ level, the fundamental output of the first narrow-band laser was used and the second laser was frequency doubled in a BBO crystal. The tunable laser ($\tilde{\nu}_3$) was reflected (unfocused) into the excitation region with an average pulse energy of ca. 400 μJ / pulse and a beam diameter of ca. 4 mm.

The two excitation laser beams intersected a skimmed supersonic expansion of pure argon (spectroscopy grade purity, Pangas) at right angle. The gas nozzle (General Valve, series 9) and the skimmer (Beam Dynamics) had an orifice of 1 mm. The distance between nozzle and skimmer and between skimmer and excitation region was 2 cm and 7 cm, respectively. The nozzle stagnation pressure was 2 bar and the opening time of

Figure 2. Schematic diagram of the experimental setup used for the resonance-enhanced two-photon excitation of Ar($3p^6\ ^1S_0$) via the $4s'[1/2]_1$ intermediate level.

the nozzle ca. $250\ \mu\text{s}$. The polarization of the VUV laser was chosen to be parallel to the z direction (see figure 1b). The relative polarization of the second excitation laser with respect to the polarization of the VUV laser was adjusted by rotating the polarization of the second excitation laser beam in the xz plane, using an angle-tunable half-wave plate. To record spectra of transitions to autoionizing levels with $M_J = 0$ (± 1) the angle θ between the polarization vectors in the excitation region was set at 0° (90°). The uncertainty in the angle could be estimated to be about 5° by monitoring the Ar^+ signal resulting from excitation to the $3p^5\ 15p'[1/2]_0$ autoionization resonance as a function of the position of the half-wave plate, exploiting the fact that this transition is forbidden for a perpendicular arrangement of the polarization vectors of the two excitation laser beams.

The photoexcitation region and the adjacent linear time-of-flight (TOF) mass spectrometer were surrounded by a double layer of magnetic shielding. The ions generated by photoexcitation were extracted with a pulsed electric field of ca. $170\ \text{V/cm}$ applied $100\ \text{ns}$ after photoexcitation. The extracted ions were detected using a microchannel-plate (MCP) detector at the end of the TOF tube. Spectra of autoionizing Rydberg states of argon were recorded by measuring the integral of the Ar^+ signal in the TOF spectra as a function of the wavenumber $\tilde{\nu}_3$ of the second excitation laser using a $500\ \text{MHz}$ digital oscilloscope. The wavenumber $\tilde{\nu}_3$ was calibrated to an accuracy of better than $100\ \text{MHz}$ by recording simultaneously a laser-induced-fluorescence spectrum of molecular iodine at wavenumbers above $15\ 000\ \text{cm}^{-1}$, and to an accuracy of $200\ \text{MHz}$ using a wavemeter (HighFinesse, WS6/200) below $15\ 000\ \text{cm}^{-1}$.

Additionally, transmission signals of the cw output of the tunable ring dye laser through two confocal étalons of different free spectral ranges were recorded for the calibration of relative wavenumbers.

3. Theory

The photoionization cross sections were calculated with the CIPFCP method applied by us earlier (Petrov *et al* 2006a, Wright *et al* 2008, Petrov *et al* 2009) to similar problems. This approach takes into account the relativistic compression of the atomic core and the spin-orbit interaction within the Pauli-Fock approximation (Kau *et al* 1997). Many-electron effects are accounted for by including all single- and double-electron excitations, both for the initial and the final states. The atomic orbitals are computed with inclusion of a core polarization potential (Petrov *et al* 1999). The Slater integrals entering the calculation of the core polarization potential, the energy levels and the transition amplitudes are corrected via the technique of effective operators (Petrov *et al* 2003, Petrov *et al* 2006a). The approach used in (Petrov *et al* 2006a, Wright *et al* 2008, Petrov *et al* 2009) yields cross sections which - when computed in the length and the velocity gauge - differ by 5-10%. In this paper, we only show the cross sections computed in the length gauge.

Theoretical details were described in (Petrov *et al* 2006a, Wright *et al* 2008, Petrov *et al* 2009). Here, we only present the main features of the calculations and introduce the principal equations and abbreviations. The total photoionization cross section for the $i_0 \rightarrow f_c$ transition is given by:

$$\sigma_{i_0}^{f_c}(\omega) = \sum_{\ell, j, J} \sigma_{i_0}^{f_c \ell j J}(\omega) \quad (1)$$

where i_0 denotes the initial state and $f_c \ell j J$ describes partial waves in the final state (f_c and ℓj denote the quantum numbers of the core and photoelectron, respectively, and J is their total angular momentum). The partial cross section $\sigma_{i_0}^{f_c \ell j J}(\omega)$ describing the contribution of the individual partial waves $|f_c \ell j J\rangle$ to the f_c -specific partial cross section $\sigma_{i_0}^{f_c}(\omega)$ is:

$$\sigma_{i_0}^{f_c \ell j J}(\omega) = \left| \langle \overline{f_c \ell j J E} \| \mathbf{D} \| i_0 \rangle \right|^2 = \left| d_{i_0}^{f_c \ell j J}(\omega) + \sum_i \frac{\langle f_c \ell j J E | \mathbf{H}^{ee} | \bar{i} \rangle}{E - E^{(i)}} D^{(i)}(\omega) \right|^2, \quad (2)$$

where the bar over the wave function of the final state $|\overline{f_c \ell j J E}\rangle$ indicates that the continuum wave function $|f_c \varepsilon \ell j J E\rangle$ is modified by the interaction with the resonances; $\mathbf{D}$ and $\mathbf{H}^{ee}$ are the electric dipole and Coulomb operators, respectively; $D^{(i)}(\omega)$ is the complex transition amplitude to the resonant state $|\bar{i}\rangle$, modified by the interaction between the resonances via the continua $|f_c \varepsilon \ell j J E\rangle$. The wave functions of the

resonances $|\bar{i}\rangle$ were calculated as described in (Wright *et al* 2008, Petrov *et al* 2009). The continuum wave functions $|f_c \varepsilon \ell j J E\rangle$, determining the amplitude $d_{i_0}^{f_c \ell j J}(\omega)$, were computed taking into account the mixing between continuum channels by numerically solving equations (4.34) and (4.35) in the article of Starace (1982). The first term in the transition amplitude (2) describes the nonresonant transition into the continuum, whereas the sum describes the influence of the ARS on the cross section.

In order to compute the dependence of the photoionization cross sections on the angle θ between the electric field vectors of the exciting and ionizing linearly-polarized lasers in the resonant two-colour excitation sequence, it is useful to introduce J -specific partial ionization cross sections:

$$\sigma_{i_0}^{f_c J}(\omega) = \sum_{\ell, j} \sigma_{i_0}^{f_c \ell j J}(\omega). \quad (3)$$

Note that the rather cumbersome designations in equations (1–3) can be substantially shortened for initial levels involving the excited electron in an s-orbital, i.e. $i_0 = 3p_j^5 ns[K]_{J_0}$, because some quantum numbers can be omitted: $K = j$ and $J_0 = 1$ for all cases considered here. Moreover, instead of indicating j , the usual designation ‘prime’ for $j = 1/2$ is used. Consequently, instead of, e.g., the designation $\sigma_{3p_{1/2}^5 ns[1/2]_1}^{3p_{1/2}^5 \varepsilon p_{3/2} J=2}$ the short designation $\sigma_{ns'}^{p' J=2}$ can be used (the total angular momentum of the p-photoelectron can also be omitted because it is determined uniquely in this case).

4. Results and discussion

Before we describe the new results, we summarize the prior experimental and theoretical knowledge on the basic properties of the np' and nf' resonances in Ar. The quantum defects μ and the reduced widths Γ_r of the $np'[1/2]_{0,1}$, $np'[3/2]_{1,2}$, and $nf'[5/2]_{2,3}$ series, as determined by experiments (Koeckhoven *et al* 1995, Peters *et al* 2005, Petrov *et al* 2006a, Wright *et al* 2008, Lee *et al* 2008) are compared in table 1 with the theoretical results of Petrov *et al* (2006a) (for earlier work, see citations in these references). The reduced width is defined by $\Gamma_r = (n - \mu)^3 \Gamma_n$ where Γ_n denotes the natural resonance width which depends on the quantum numbers n , l , K , and J . The table also includes the experimental and theoretical results obtained in the present work. The earlier experiments involved single-photon excitation from the metastable Ar($4s[3/2]_2$, $4s'[1/2]_0$) levels (Petrov *et al* 2006a, Wright *et al* 2008), four-photon excitation (Koeckhoven *et al* 1995) as well as two-colour two-photon excitation of ground state Ar via several odd-parity intermediate levels with $J = 1$ (Lee *et al* 2008).

As expected for general reasons (Petrov *et al* 2002), the nf' resonances are much narrower than the np' resonances. The $np'[3/2]_{1,2}$ resonances are much sharper than the $np'[1/2]_{0,1}$ resonances. Overall, there is a satisfying agreement between the existing experimental and theoretical data, but on a quantitative level, the calculated reduced widths differ from the measured values by up to about 40%. The calculation of accurate

Table 1. Theoretical and experimental reduced widths [cm^{-1}] and quantum defects for p- and f-Rydberg states of Ar. The numbers in parentheses represent the experimental uncertainty in units of the last digit.

n	$np'[1/2]$				$np'[3/2]$			
	$J = 0$		$J = 1$		$J = 1$		$J = 2$	
	Γ_r	μ	Γ_r	μ	Γ_r	μ	Γ_r	μ
11 ^{a)}	4454	1.601	4479	1.675	481	1.6781	447	1.6686
12 ^{a)}	4487	1.600	4378	1.675	481	1.6775	447	1.6680
14 ^{a)}	4507	1.599	4287	1.674	481	1.6769	447	1.6674
16 ^{a)}	4511	1.599	4262	1.674	482	1.6765	448	1.6671
11–13 ^{b)}	4050 (560)	1.614(8)						
13,14 ^{c)}			3600 (200)	1.675(3)			700 (200)	1.668(3)
11 ^{d)}			3015 (1100)	1.6762(9)	533 (40)	1.6792(9)	321 (110)	1.6686 ^{e)}
11–16 ^{f)}	2549– 4145	1.616(1)	≈ 2920 ^{g)}		≈ 320 ^{g)}	1.688(1)		1.677(2)
15 ^{h)}	3920 (300)	1.6140(5)					340 (40)	1.67651(8)
n	$nf'[5/2]$				$nf'[7/2]$			
	$J = 2$		$J = 3$		$J = 3$		$J = 4$	
	Γ_r	μ	Γ_r	μ	Γ_r	μ	Γ_r	μ
9 ⁱ⁾	182	0.0077	192	0.0079	81	0.0083	79	0.0082
12 ^{a)}	181	0.0078						
10 ^{b)}		0.010(5)						0.010(5)
9 ^{j)}			166(3)	0.01122(3)				
10 ^{j)}			158(4)	0.01144(3)				
9–11 ^{k)}	130– 324	0.011(1)						
13,14 ^{h)}	155(20)	0.01108(6)						

^{a)} Present calculations^{b)} Experiment (four-photon excitation) (Koeckhoven *et al* 1995)^{c)} Experiment (one-photon excitation of metastable Ar) (Peters *et al* 2005)^{d)} Experiment (one-photon excitation of metastable Ar) (Wright *et al* 2008)^{e)} Experimental quantum defect set equal to the calculated value^{f)} Experiment (two-photon excitation) (Lee *et al* 2008)^{g)} Estimates for $n = 11$ (Lee *et al* 2008)^{h)} Present experiment (two-photon excitation)ⁱ⁾ Calculation (Petrov *et al* 2006a)^{j)} Experiment (one-photon excitation of metastable Ar) (Petrov *et al* 2006a)^{k)} Experiment (two-photon excitation) (Lee *et al* 2008). The width of the nf' resonance peaks is substantially broadened by the 0.25 cm^{-1} laser width; the corrected linewidths range from 0.13 cm^{-1} to 0.44 cm^{-1} , yielding the quoted range for the reduced widths.

resonance positions E_n is challenging (the energies are given relative to the upper ionization limit $I_{1/2}$, i.e. $I_{1/2} - E_n = \text{Ry}/(n - \mu_\ell)^2$). Except for the $[1/2]_0$ levels, the calculation of which poses special problems (Petrov *et al* 2006b), the agreement between the experimental and the calculated values of the quantum defects can be considered as good. In particular the energetic sequence of the four np' resonances is well described and was helpful for the analysis and assignment of measured resonance spectra (Wright *et al* 2008).

The recent results of Lee *et al* (2008) and our present data have significantly broadened the experimental data base for the np' and nf' resonances. Note that - compared to our work - the measurements of Lee *et al* were carried out with substantially broader laser width (in most cases 0.25 cm^{-1}) and lower accuracies in the wavelength determination of the ionizing laser. Lee *et al* (2008) did not quote individual error bars for their widths and quantum defects. The uncertainties of the quantum defects of Lee *et al* (2008) listed in table 1 reflect the scatter of their values for the respective range of n . The reduced widths reported by Lee *et al* (2008) for the $np'[1/2]_0$ and the $nf'[5/2]_2$ resonances fluctuate strongly and nonsystematically as a function of n ; therefore, we only quote the interval within which the measured values are located.

4.1. Ionization from the levels $4s[3/2]_1$, $4s'[1/2]_1$, $5s[3/2]_1$ and $5s'[1/2]_1$

In figure 3 we present the computed ionization cross sections in the region of the $12f'[5/2]_2$, $14p'[1/2]_{0,1}$, and $14p'[3/2]_{1,2}$ resonances (left-hand side) together with the J -specific continuum cross sections for producing the Ar^+ ion in the $^2\text{P}_{1/2}$ final state (right-hand side). The panels a), b), c), and d) represent the results for the four intermediate levels $4s[3/2]_1$, $4s'[1/2]_1$, $5s[3/2]_1$ and $5s'[1/2]_1$, respectively, as calculated for unpolarized atomic states (i.e., for measurements at the angle $\theta = 54.7^\circ$ between the polarization vectors of the two laser beams). The non-resonant photoionization cross section is rather small from the $4s[3/2]_1$ and $4s'[1/2]_1$ levels (around 0.2 Mb), and the weakness of the s-p amplitude is attributed to the close proximity of a Seaton-Cooper minimum (Kau *et al* 1998). The non-resonant cross section is substantially higher for the $5s[3/2]_1$ level (about 1 Mb) and the $5s'[1/2]_1$ level (about 0.6 Mb).

Next, we consider the energy dependence of the J -specific partial ionization cross sections $\sigma_{i_0}^{p'J}(\omega)$ $J = 0, 1, 2$ and $\sigma_{i_0}^{f'J}(\omega)$ $J = 2$ ($\text{Ar}^+(^2\text{P}_{1/2})$ formation; right panels) which - when extrapolated to the range below the $\text{Ar}^+(^2\text{P}_{1/2})$ threshold - provide a measure of the energy-integrated oscillator strength of the resonant part of the cross sections in the autoionization region (we note that for $J = 1$ the cross section $\sigma_{i_0}^{p'J}$ displayed in figure 3 is the sum of the partial cross sections $\sigma_{i_0}^{p'_{1/2}J}$ and $\sigma_{i_0}^{p'_{3/2}J}$ whereas for other J values the total angular momentum of the photoelectron is determined uniquely). The narrow $np'[3/2]_2$ resonance is expected to be the most intense feature in the photoionization spectra recorded from the $4s[3/2]_1$ level (figure 3a), as observed (resonant peak cross section above non-resonant background about 3.6 Mb), whereas the $J = 0$ resonance appears as a weak window-type resonance. When photoionization

Figure 3. Left panels: Computed $12f'$, $14p'$ ARS of Ar, excited from the unpolarized levels $4s[3/2]_1$ (a), $4s'[1/2]_1$ (b), $5s[3/2]_1$ (c) and $5s'[1/2]_1$ (d). Right panels: corresponding $\epsilon f'$ and $\epsilon p'$ continuum cross sections for $\text{Ar}^+(^2P_{1/2})$ formation. The energies are given with respect to the $^2P_{1/2}$ ionization threshold.

occurs from the $4s'[1/2]_1$ level, the broad $np'[1/2]_0$ resonance is the dominant spectral feature (figure 3b, peak cross section about 4 Mb), the $J = 1, 2$ contributions being strongly attenuated by the Seaton-Cooper minima in these channels. In the spectra recorded from the $5s[3/2]_1$ intermediate level, the $np'[3/2]_2$ resonance is again expected to be prominent (peak cross section above continuum about 8 Mb), but the strength of the $np'[1/2]_0$ resonance, which has a dispersive lineshape (Fano shape parameter $q = 1.22$), is also substantial. The $J = 1$ resonances are again weak. Finally, in the spectra recorded from the $5s'[1/2]_1$ level, the $np'[3/2]_2$ resonance (peak cross section about 104 Mb) and the $np'[1/2]_0$ resonance (peak cross section about 16 Mb) are much stronger than in the spectra from $5s[3/2]_1$ and have near-Lorentzian profiles.

The narrow $nf'[5/2]_2$ resonances (reduced width about 2.2 times smaller than for the $np'[3/2]_2$ resonances) are observed as a result of electron correlation effects such as s-d mixing and other correlations discussed in (Petrov *et al* 2003, Petrov *et al* 2006a)). As also reflected in the $\varepsilon f' J = 2$ continuum cross sections (full lines in the right panels), they are weak from the $4s'[1/2]_1$ level (peak cross section above continuum about 0.05 Mb), but much stronger and similar in strength to that of the $np'[3/2]_2$ resonances from the $4s[3/2]_1$ level (about 8 Mb) and the $5s[3/2]_1$ level (about 10 Mb), and very strong from the $5s'[1/2]_1$ level (about 106 Mb). In all cases, the $nf'[5/2]_2$ resonances have near-Lorentzian shapes.

In the experiments, the spectra of the autoionizing Ar(np' , nf') resonances were recorded from three excited Ar levels, namely $4s'[1/2]_1$, $3d[1/2]_1$, and $5s[3/2]_1$ which were reached from the Ar ground state by linearly-polarized VUV radiation. Data were taken with parallel (0°) and perpendicular (90°) arrangement of the electric vectors of the two radiation fields. In this way, the $J = 1$ ARS (0°) or the $J = 0$ ARS (90°) could be selectively ‘switched off’ according to the expressions (see, e.g., (Petrov *et al* 2006b)):

$$\begin{aligned}\sigma(0^\circ) &= 3 \sigma^{J=0} + \frac{6}{5} \sigma^{J=2} \\ \sigma(90^\circ) &= \frac{3}{2} \sigma^{J=1} + \frac{9}{10} \sigma^{J=2},\end{aligned}\tag{4}$$

where σ^J is defined in equation (3) (the subscript i_0 is omitted to simplify the notation).

In terms of the cross sections $\sigma(0^\circ)$ and $\sigma(90^\circ)$, the total cross section for unpolarized atoms $\sigma_{tot} = \sigma(54.7^\circ)$ is given by

$$\sigma_{tot} = \frac{1}{3} \sigma(0^\circ) + \frac{2}{3} \sigma(90^\circ)\tag{5}$$

Figure 4 displays the photoionization spectra of Ar recorded via the $4s'[1/2]_1$ (a,b) and $5s[3/2]_1$ (c,d) intermediate levels for perpendicular (a,c) and parallel (b,d) polarizations, respectively. The energy range includes the $13f'$, $15p'$, and $14f'$ resonances. As expected, the broad $15p'[1/2]_0$ resonance is almost completely absent from the two spectra (a,c) measured with the perpendicular polarization arrangement. The suppression, ideally 100%, amounts to about 98.5%; the remaining intensity of the

Figure 4. Photoionization cross sections for polarized $4s'[1/2]_1$ and $5s[3/2]_1$ levels of Ar, as measured for parallel (b,d) and perpendicular (a,c) electric vectors of the linearly-polarized light beams. The energies are given with respect to the $^2P_{1/2}$ ionization threshold.

$J = 0$ resonance in (a,c) is due to a slight imperfection in the polarization of the VUV radiation. In the spectra (a,c), which should exhibit the $J = 1$ resonances $15p'[1/2]_1$ and $15p'[3/2]_1$, such contributions are not observable within the sensitivity limit of the experiment. The $15p'[3/2]_2$ resonance is clearly present in the spectra (c,d), excited from $5s[3/2]_1$, but it is absent in the spectra (a,b), excited from $4s'[1/2]_1$. The shape of the $15p'[1/2]_0$ resonance is rather different in the two cases (b,d), corresponding to Fano q parameters of about +6 (b) and +1.5 (d).

The average values of the reduced widths and the quantum defects, as determined from the experimental spectra by means of Fano-type lineshape analyses of the $15p'[1/2]_0$, $15p'[3/2]_2$, $13f'[5/2]_2$, and $14f'[5/2]_2$ resonances, are summarized in table 1. The reduced width of the $15p'[3/2]_2$ resonance ($340(40) \text{ cm}^{-1}$) agrees with the value determined by Wright *et al* (2008) and that of the $nf'[5/2]_2$ resonances ($155(20) \text{ cm}^{-1}$, $n = 13, 14$) corresponds closely to that measured by Peters *et al* (2005) for $n = 9, 10$. For the broad $15p'[1/2]_0$ resonance our measured reduced width $3920(300) \text{ cm}^{-1}$ agrees with the value determined from four-photon excitation spectra of ground state Ar by

Figure 5. Comparison between measured (right panels) and computed (left panels) photoionization cross sections for unpolarized (a) $4s'[1/2]_1$, (b) $5s[3/2]_1$ and (c) $5s'[1/2]_1$ levels of Ar. The experimental data for $5s'[1/2]_1$ are from Lee *et al* (2008)

325 (Koeckhoven *et al* 1995) for the series members $n = 11 - 13$, and it is 13% lower
 326 than the theoretical prediction. Lee *et al* (2008) determined the width for the $n =$
 327 11 – 16 members of the $np'[1/2]_0$ series: the corresponding reduced widths vary non-
 328 systematically over the range 2549 – 4145 cm^{-1} (no uncertainties for the individual

Table 2. Comparison of computed and experimentally determined Fano q parameters of the resonance lineshapes, shown in figures 5 and 7

Resonance		Intermediate level			
		$4s'[1/2]_1$	$5s'[1/2]_1$ ^{a)}	$5s[3/2]_1$	$3d[1/2]_1$
$nf'[5/2]_2$	Theor.	15.8	62	-11.7	-22.2
	Exp.	$ q > 10$	$ q > 15$	-10(3)	-15(5)
$np'[3/2]_2$	Theor.	$ q > 500$	61	31	-15.3
	Exp.		$ q > 50$	$ q > 50$	-30(15)
$np'[1/2]_0$	Theor.	5.3	12.8	1.22	
	Exp.	6.5(5)	13(2)	1.7(3)	

^{a)} Fano-type lineshape analysis of experimental data measured by Lee *et al* (2008) (see figure 5c.)

widths were quoted).

In figure 5, we compare the experimental (right panels) and theoretical (left panels) spectra of the $nf'[5/2]_2$ and np' resonances for the (a) $4s'[1/2]_1$, (b) $5s[3/2]_1$ and (c) $5s'[1/2]_1$ level (the experimental $5s'$ data are from Lee *et al* (2008)). The cross sections are displayed as a function of $-\mu$, i.e. a negative quantum defect used as scaled energy variable. In this way spectra measured or calculated for different principal quantum numbers can be compared on a common scale. Moreover, the differences between the experimental and the theoretical quantum defects are directly apparent. In panels (a)–(c), the total (unpolarized) experimental cross sections have been computed from the data measured at 0° and 90° using the equations (4) and (5) given above. Good overall agreement between theory and experiment is observed in the lineshapes and strengths of the different contributing resonances. Even the relative intensities for the np' and the nf' resonances are reproduced to within a factor of three. To allow for a quantitative comparison between the computed and measured lineshapes shown in figure 5 and in figure 7, we list in Table 2 the respective Fano shape parameter q (for its definition, see, e.g., Wright *et al* (2008)).

Finally, we discuss the behaviour of the cross sections in the vicinity of Seaton-Cooper minima which occur in the $(\varepsilon/n)p'$ -channels (see figure 3). In the $5s' \rightarrow \varepsilon p' J$ transitions, the minima are located at 0.55 eV above the $\text{Ar}^+ \ ^2P_{1/2}$ threshold for $J = 1$ and at 0.85 eV for $J = 2$. The $5s \rightarrow \varepsilon p' J$ transitions do not exhibit a Seaton-Cooper minimum, but the $J = 1$ channel is weak; correspondingly, the $15p' J = 1$ resonances are not observed in the experimental spectra recorded from the $5s[3/2]_1$ level.

In the $4s' \rightarrow \varepsilon p' J$ channels, the minima are shifted to the energy range of the autoionizing resonances (see figure 3b); they are depicted on an enlarged scale in figure 6a. In this figure, the cross sections σ_n for the discrete states were obtained from $\sigma_n = 4\pi^2 \alpha a_0^2 \text{Ry} f_n / (dE_n/dn)$ (i.e. the equivalent for the discrete region of equation (2.14) in (Fano and Cooper 1968) which describes the continuum photoionization cross

Figure 6. a) Cross sections for the $4s'[1/2]_1 \rightarrow n/\varepsilon p'[K]_{1,2}$ transitions (the full curves represent spline fits connecting the data points, computed at discrete bound energies and a grid of continuum energies). b) n -dependence of the lineshapes for the $4s'[1/2]_1 \rightarrow np'$ transitions in the vicinity of the Seaton-Cooper minima.

section); here $dE_n/dn = 2Ry/(n - \mu)^3$ and α , a_0 , Ry, and f_n denote the fine-structure constant, Bohr radius, Rydberg energy unit, and the computed oscillator strength for the $4s' \rightarrow np'[K]_J$ transitions, respectively. The cross sections σ_n are interpolated using a spline fit to make the energy dependence more easily recognizable.

The broad $p'[1/2]_1$ resonances mainly contribute to the ‘background’. The appearance of the sharp $np'[3/2]_1$ and $np'[3/2]_2$ resonances is affected by the strong n (i.e. energy) dependence of their cross sections. The experimental photoionization spectra obtained from the $4s'[1/2]_1$ intermediate level confirm the predicted near-zero strength of the $np'[3/2]_1$ resonance at $n = 15$. The $15p'[3/2]_2$ resonance is also not observed experimentally while the calculations predict the minimum to occur at lower energies (at $n = 11$).

The predicted lineshapes of selected np' resonances are depicted in figure 6b. They clearly demonstrate that the strong variation of the resonance spectra at, or very close to,

Figure 7. Comparison between the computed (a) and measured (b) photoionization cross sections for the unpolarized Ar($3d[1/2]_1$) level in the $13f'$, $15p'$ autoionization region. In the right panel, the calculated $\epsilon f'$ and $\epsilon p'$ continuum cross sections for $\text{Ar}^+(^2P_{1/2})$ formation are shown.

specific n -values can serve as a sensitive probe for the energy location of such a minimum in a particular channel and enable a rigorous test of the theoretical approaches.

4.2. Ionization from the $3d[1/2]_1$ level

The computed and measured cross sections for photoionization from the intermediate $3d[1/2]_1$ level are compared in figure 7 in the region of the $13f'$ and $15p'$ resonances. As predicted by the calculation, the f' resonance (peak cross section about 2500 Mb) dominates, reflecting the fact that the direct $d-f'$ dipole amplitude is much stronger than the $d-p'$ amplitude. In the $15p'$ spectrum, the $J = 2$ contribution is the strongest (computed peak cross section about 57 Mb above the continuum level of about 27 Mb). The experimental ratio of 20 between the $13f'[5/2]_2$ and the $15p'[3/2]_2$ peak ion yields (continuum subtracted) and of 2.7 between the $15p'[3/2]_2$ peak and the continuum cross section are in qualitative agreement with the respective calculated cross sections ratios of 44 and 2.1. We note that in view of the very high nf' peak cross section, the heights of the experimental nf' peaks – as compared to those of the np' resonances – may be too small as a result of saturation effects (typical fluence of the laser pulses around 5×10^{15} photons/cm²). This is also indicated by the somewhat larger reduced width $195(25)$ cm⁻¹ of the $13f'[5/2]_2$ and $14f'[5/2]_2$ resonances determined from experimental data such as those shown in figure 7b.

The dominance of the $f'[5/2]_2$ channel is also reflected in the computed partial continuum cross sections for $\text{Ar}^+(^2P_{1/2})$ formation, as depicted in the right upper panel of figure 7. The $\epsilon f'$, $J = 2$ cross section exceeds that of the strongest $\epsilon p'$ channel with $J = 2$ by about a factor of 20. For all four continua, the partial cross sections decrease

with rising photoelectron energy; therefore, no Seaton-Cooper minima are expected to occur in the energy range of the nf' and np' resonances and the appearance of the lineshapes seen for the $13f'$ and $15p'$ resonances should be characteristic for all principal quantum numbers in the autoionization region.

4.3. Ionization from the levels $7s'[1/2]_1$ and $8s[3/2]_1$

Ionization of ground state Ar atoms through several odd parity excited $J = 1$ levels has been investigated by Lee *et al* (2008) by combined synchrotron radiation and laser excitation. Some of their findings have already been discussed above. We found their results for the intermediate levels $7s'[1/2]_1$ and the $8s[3/2]_1$ of special interest, since these two excited levels are nearly degenerate (level separation only $53.667 \text{ cm}^{-1} = 6.654 \text{ meV}$). This near-degeneracy is due to the fact that the spin-orbit splitting of the core is almost equal to the difference in binding energies between the $7s$ and $8s$ Rydberg states. As a result of this energetic proximity, these levels are strongly mixed, and this mixing influences the appearance of the respective ionization spectra. As a consequence it is not possible (as tried by Lee *et al* (2008)) to infer the lineshapes of the autoionizing np' resonances for either of the two intermediate levels from those observed for lower-lying non-degenerate $ms'[1/2]_1$ or $ms[3/2]_1$ levels with $m < 7$.

In figure 8 we present the theoretical results for unpolarized intermediate levels. In panels a) and b) we show the lineshapes which are obtained when the two respective intermediate levels $7s'[1/2]_1$ and $8s[3/2]_1$ are fully described (including their mixing). In contrast, the lineshapes in panels c) and d) were obtained by assuming that the states are ‘non-interacting’. In terms of the non-interacting states (subscript ‘*ni*’) the full wave functions can be written as:

$$\begin{aligned} |7s'\rangle &= 0.849 |7s'\rangle_{ni} + 0.528 |8s\rangle_{ni} \\ |8s\rangle &= -0.528 |7s'\rangle_{ni} + 0.849 |8s\rangle_{ni} \end{aligned} \quad (6)$$

The cross sections for the non-interacting states $|7s'\rangle_{ni}$ and $|8s\rangle_{ni}$ are very different in both the size and the lineshapes (q parameters) of the narrow $14p'[3/2]_{2,1}$ and the broad $14p'[1/2]_0$ resonances (the broad $14p'[1/2]_1$ resonance is weak and spread around the sharp $[3/2]_{2,1}$ lines). The non-interacting $|7s'\rangle_{ni}$ and $|8s\rangle_{ni}$ states are almost purely jj -coupled with a $j_c = 1/2$ and a $j_c = 3/2$ core, respectively.

Thus, the $7s'_{ni} \rightarrow 14p'$ core-conserved transition is about 40 times stronger than the $8s_{ni} \rightarrow 14p'$ core-changed transition (cf figures 8c and 8d). Therefore, the photoionization cross sections from the $|7s'\rangle$ and $|8s\rangle$ levels (6) have predominantly the character of the $|7s'\rangle_{ni}$ state. The most remarkable consequence of this mixing is the observation that the $np'[1/2]_0$ resonance appears as a peak in the spectra excited from both the $|7s'\rangle$ and $|8s\rangle$ states (see figures 8a and 8b), whereas for the non-interacting $|8s\rangle_{ni}$ state the $np'[1/2]_0$ ARS appears as a weak, slightly asymmetric window resonance due to destructive interference between the $\langle ms|\mathbf{r}|np\rangle$ and $\langle ms|\mathbf{r}|mp\rangle \langle mp|V(3p3p)|np\rangle$

Figure 8. Left-hand side: Ar($14p'$) autoionization spectra, excited from the unpolarized $7s'[1/2]_1$ and $8s[3/2]_1$ levels, as computed with mixing a), b) and without mixing (non-interacting states) c), d) (see text). Right-hand side: Corresponding continuum cross sections for producing Ar^+ ions in the $^2P_{1/2}$ state at photoelectron energies of 0 - 1000 meV. The energies are given with respect to the $^2P_{1/2}$ ionization threshold.

amplitudes (reflecting electron correlation effects), as first revealed for the case of Ne by Petrov *et al* (2006b). Thus, the Lorentzian-like lineshape of the $28p'[1/2]_0$ resonance observed by Lee *et al* (2008) following excitation from both $|7s'\rangle$ and $|8s\rangle$ cannot be interpreted as indicating the absence of the interference identified earlier by Petrov *et al* (2006a,b). Instead, it results from the strong mixing between the $|7s'\rangle_{ni}$ and $|8s\rangle_{ni}$ states.

5. Conclusions

Experimental and theoretical spectra of even Ar(np' $J = 0, 1, 2$; nf' $J = 2$; n around 14) autoionizing Rydberg states, accessed from the intermediate levels $4s[3/2]_1$, $4s'[1/2]_1$, $5s[3/2]_1$, $5s'[1/2]_1$, $3d[1/2]_1$, $7s'[1/2]_1$, and $8s[3/2]_1$, and the widths, energy locations and lineshapes of these resonances are discussed. The computed reduced widths agree with the experimental values to within about 40% or better. The calculated quantum defects differ from the measured values by -0.009 for $np'[3/2]_2$, -0.015 for $np'[1/2]_0$, and by about -0.003 for the $nf'[5/2]_{2,3}$ series. The computed resonance profiles are in good to excellent agreement with the measured lineshapes. Moreover, the computed *absolute* values of the resonance and continuum cross sections are reported.

Seaton-Cooper minima in several $(n/\varepsilon)p'$ channels are observed and the n -dependence of the resonance profiles around the minima is discussed in comparison with the experimental observations. The strong variation of the resonance spectra around specific n -values serves as a sensitive probe for the energy location of such a minimum in a particular channel and enables a rigorous test of the theoretical approaches.

The spectra excited from the $7s'[1/2]_1$ and $8s[3/2]_1$ levels are analyzed in detail. It was found that the lineshapes of the np' resonances excited from these levels are greatly influenced by (a) the strong mixing between the $7s'[1/2]_1$ and $8s[3/2]_1$ levels and (b) the interference between different excitation pathways reflecting electron correlation effects. Recent observations of the $7s' \rightarrow np'$ and $8s \rightarrow np'$ ARS spectra by Lee *et al* (2008) were interpreted on the basis of these findings.

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