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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 \(3p_{1/2}^5 4s'[1/2]_1\), \(3p_{1/2}^5 5s[3/2]_1\) 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 $Rg m^5p_{3/2}nℓ'[K']$ autoionizing Rydberg states (ARS) which belong to series converging on the higher ionization threshold Rg$^+$ $mp_{1/2}^5$ and decay to Rg$^+$ $mp_{5/2}$$\varepsilon$-$ℓ$, $J$ 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 $\vec{ℓ}$ 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 (CIPFC) 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 $⟨3s|\mathbf{r}|np⟩$ and the intershell $⟨3s|\mathbf{r}|3p⟩$ $(3p|V(2p2p)|np)$ amplitudes. This interference turned out to be constructive in the $3s' → np'$ transitions and destructive in the $3s → np'$ 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 predictons.

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]1 and 5s[3/2]1 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(3p6 1S0) 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 = ±1 and the J = 0 series (i) is not accessible. When they are chosen to be parallel, excitation
Autoionizing dynamics of Ar (np', nf') resonances

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 \( \begin{bmatrix} 1 & 1 & 1 \\ 0 & 0 & 0 \end{bmatrix} \) 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 \(n'\) and \(np'\) Rydberg states just above the \(2^3\)P \(3/2\) ionization threshold of argon. The VUV wavenumbers \((\tilde{\nu}_{\text{VUV}} = 2\tilde{\nu}_{\text{UV}} + \tilde{\nu}_2)\) at \(111\,818.03\,\text{cm}^{-1}\), \(114\,975.02\,\text{cm}^{-1}\) and \(95\,399.83\,\text{cm}^{-1}\) which were used to drive the transitions from the \(1^1\)S \(0\) 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 \(2^3\)P \(3/2\) ionization threshold were recorded by monitoring the Arg \(^+\) 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 \(0.04\,\text{cm}^{-1}\) in the fundamental, was frequency doubled in a \(\beta\)-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 \(\approx 150\,\text{MHz}\) 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 \(\mu\text{J}/\text{pulse}\) 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
the nozzle ca. 250 µs. 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 \( \theta \) 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 \( \text{Ar}^+ \) 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 V/cm applied 100 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 \( \text{Ar}^+ \) signal in the TOF spectra as a function of the wavenumber \( \tilde{\nu}_3 \) of the second excitation laser using a 500 MHz digital oscilloscope. The wavenumber \( \tilde{\nu}_3 \) was calibrated to an accuracy of better than 100 MHz by recording simultaneously a laser-induced-fluorescence spectrum of molecular iodine at wavenumbers above 15000 cm\(^{-1}\), and to an accuracy of 200 MHz using a wavemeter (HighFinesse, WS6/200) below 15000 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:

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

where $i_0$ denotes the initial state and $f_c\ell j J$ describes partial waves in the final state ($f_c$ and $\ell j$ 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:

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

where the bar over the wave function of the final state $| f_c\ell j J \rangle$ indicates that the continuum wave function $| f_c\varepsilon \ell j J \rangle$ 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 $| i \rangle$, modified by the interaction between the resonances via the continua $| f_c\varepsilon \ell j J \rangle$. The wave functions of the
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resonances $|i\rangle$ were calculated as described in (Wright et al. 2008, Petrov et al. 2009). The continuum wave functions $|f_c\ell jJE\rangle$, determining the amplitude $d_{i0}^{f_c\ell j J}(\omega)$, 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 $\theta$ 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:

$$\sigma_{i0}^{f_c \ell j J}(\omega) = \sum_{\ell j} \sigma_{i0}^{f_c \ell j J}(\omega). \quad (3)$$

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.

$$i_0 = 3p^3 ns[K]_{J_0},$$

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^3 ns\[1/2\]}^{3p^3 \ell s\[3/2\]1} J=2$ the short designation $\sigma_{ns'}^{\ell s\[3/2\]} 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 $\mu$ and the reduced widths $\Gamma_r$ 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 $\Gamma_n$ 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.

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<td>0.01108(6)</td>
<td>324</td>
<td>155(20)</td>
<td>0.01108(6)</td>
</tr>
</tbody>
</table>

$^a$ 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. $I_{1/2} - E_n = \text{Ry}/(n - \mu_J)^2$). 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 $12p'[5/2]_2$, $14p'[1/2]_0,1$, 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 $^2P_{1/2}$ 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 $\sigma_{io}^{p'J}(\omega)$ $J = 0,1,2$ and $\sigma_{io}^{f'J}(\omega)$ $J = 2$ (Ar$^+ (^2P_{1/2})$ formation; right panels) which – when extrapolated to the range below the Ar$^+ (^2P_{1/2})$ 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 $\sigma_{io}^{p'J}$ displayed in figure 3 is the sum of the partial cross sections $\sigma_{io}^{p'1/2J}$ and $\sigma_{io}^{p'3/2J}$ 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 εf' and εp' continuum cross sections for Ar^+(2P_{1/2}) formation. The energies are given with respect to the 2P_{1/2} ionization threshold.
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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'[3/2]_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 εf' 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)):

\[
\sigma(0°) = 3 \sigma^{J=0} + \frac{6}{5} \sigma^{J=2}
\]

\[
\sigma(90°) = \frac{3}{2} \sigma^{J=1} + \frac{9}{10} \sigma^{J=2},
\]

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

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

\[
\sigma_{tot} = \frac{1}{3} \sigma(0°) + \frac{2}{3} \sigma(90°)
\]

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
Autoionizing dynamics of Ar ($np', nf'$) resonances

Figure 4. Photoionization cross sections for polarized 4s'\[1/2\] and 5s[3/2] 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 $^{2}P_{1/2}$ 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] and 15p'[3/2], such contributions are not observable within the sensitivity limit of the experiment. The 15p'[3/2] resonance is clearly present in the spectra (c,d), excited from 5s[3/2], but it is absent in the spectra (a,b), excited from 4s'\[1/2\]. The shape of the 15p'[1/2] 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], 15p'[3/2], 13f'[5/2], and 14f'[5/2] resonances, are summarized in table 1. The reduced width of the 15p'[3/2] resonance (340(40) cm$^{-1}$) agrees with the value determined by Wright et al (2008) and that of the nf'[5/2] resonances (155(20) 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] resonance our measured reduced width 3920(300) cm$^{-1}$ agrees with the value determined from four-photon excitation spectra of ground state Ar by...
Autoionizing dynamics of Ar ($np', nf'$) resonances

Figure 5. Comparison between measured (right panels) and computed (left panels) photoionization cross sections for unpolarized (a) 4s'[$1/2$], (b) 5s[3/2] and (c) 5s'[1/2] levels of Ar. The experimental data for 5s'[1/2] are from Lee et al. (2008) (Koeckhoven et al. 1995) for the series members $n = 11 - 13$, and it is 13% lower than the theoretical prediction. Lee et al. (2008) determined the width for the $n =$ 11 – 16 members of the $np'[1/2]_0$ series: the corresponding reduced widths vary non-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

<table>
<thead>
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<th>Resonance</th>
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<td>$5s'[1/2]_1$</td>
<td>$5s[3/2]_1$</td>
<td>$3d[1/2]_1$</td>
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<td>$nf'[5/2]_2$</td>
<td>Theor. 15.8</td>
<td>62</td>
<td>-11.7</td>
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<td>q</td>
<td>&gt; 10$</td>
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<tr>
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<td>Theor. $</td>
<td>q</td>
<td>&gt; 500$</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>Exp. $</td>
<td>q</td>
<td>&gt; 500$</td>
<td>$</td>
</tr>
<tr>
<td>$np'[1/2]_0$</td>
<td>Theor. 5.3</td>
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<td>1.22</td>
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<tr>
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<td>Exp. 6.5(5)</td>
<td>13(2)</td>
<td>1.7(3)</td>
<td></td>
</tr>
</tbody>
</table>

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

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 $Ar^+ 2P_{1/2}$ 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 $\sigma_n$ for the discrete states were obtained from $\sigma_n = 4\pi^2 a_0^2 \text{Ry} f_n/(dE_n/dn)$ (i.e. the equivalent for the discrete region of equation (2.14) in (Fano and Cooper 1968) which describes the continuum photoionization cross
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![Graph showing cross sections for the \(4s' \rightarrow (n/\epsilon)p'[K]_J\) transitions.](graph.png)

**Figure 6.** a) Cross sections for the \(4s'[1/2]_1 \rightarrow n/\epsilon p'[K]_{1,2}\) 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.

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,
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 13\( f' \) and 15\( p' \) 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 15\( p' \) 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 13\( f'[5/2]_2 \) and the 15\( p'[3/2]_2 \) peak ion yields (continuum subtracted) and of 2.7 between the 15\( p'[3/2]_2 \) 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 \( n f' \) peak cross section, the heights of the experimental \( n f' \) peaks – as compared to those of the \( n p' \) resonances – may be too small as a result of saturation effects (typical fluence of the laser pulses around \( 5 \times 10^{15} \) photons/cm\(^2\)). This is also indicated by the somewhat larger reduced width 195(25) cm\(^{-1}\) of the 13\( f'[5/2]_2 \) and 14\( f'[5/2]_2 \) 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 \( \text{Ar}^+(2\text{P}_{1/2}) \) 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 \( n'f \) 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 cm\(^{-1} \) = 6.654 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:

\[
\begin{align*}
|7s'\rangle &= 0.849 |7s'\rangle_{ni} + 0.528 |8s\rangle_{ni} \\
|8s\rangle &= -0.528 |7s'\rangle_{ni} + 0.849 |8s\rangle_{ni}
\end{align*}
\]

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 \( 7s'[1/2]_0 \rightarrow 14p' \) 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 \( \langle ms|r|np' \rangle \) and \( \langle ms|r|mp \rangle \langle mp|V(3p3p)|np' \rangle \)
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'⟩ and |8s⟩ 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'⟩_{ni} and |8s⟩_{ni} states.
5. Conclusions

Experimental and theoretical spectra of even Ar\((np', J = 0, 1, 2; nf', J = 2; n \text{ around } 14)\) 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 \((n/\epsilon)p'\) 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.

Acknowledgments

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