High-Resolution Measurements of the 3s Satellite Spectrum of Argon between 77 and 120 eV Photon Energy

H. Kossmann, B. Krässig, and V. Schmidt
Fakultät für Physik, Universität Freiburg, D-7800 Freiburg, West Germany

and

J. E. Hansen
Zeeman Laboratory, University of Amsterdam, NL-1018 TV Amsterdam, The Netherlands
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A high-resolution 3s satellite spectrum of Ar is presented, obtained at five energies between 77 and 120 eV photon energy at the positron-electron storage ring BESSY. The results are in disagreement with recent measurements by Brion *et al.* obtained at lower resolution but confirm earlier calculations by Smid and Hansen. This means that disagreements between photoelectron and $(e,2e)$ experiments persist for Ar.

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There has recently been considerable interest in the interpretation of the satellite spectrum of Ar following ionization in the 3s shell. This spectrum can be observed by use of either a photon or an electron to remove the 3s electron. The satellite spectrum is basically due to configuration interaction in the final ionic state between $3s3p^6$ and $3s^23p^4nd/\epsilon d$ states. The physical interpretation of the satellites is that they are due to the admixture of $3s3p^6$ in the different final states and it is claimed that both photoelectron spectroscopy (PES) and binary $(e,2e)$ spectroscopy measure the $3s3p^6$ amplitude by means of an intensity measurement. However, large disagreements exist between the early PES results[1,2] and the original $(e,2e)$ results[3,4] with regard to relative intensities for both Ar and Xe. In PES, except at high energy, the satellite intensity also depends on a dipole matrix element and it has been claimed[3] that the $(e,2e)$ results are more reliable. However, in 1983 Smid and Hansen[5] showed that there was agreement between *ab initio* calculations and the then-available PES results if the influence of the ϵd continuum was considered. Since then, the $(e,2e)$ measurements have been revised[6-9] and the disagreement with PES experiments for Ar has been reduced, but not removed.[6,7] For Xe, the new $(e,2e)$ measurements[8,9] have largely removed the previous disagreement between PES and $(e,2e)$ results and this is one reason that we concentrate on Ar in the present paper.

Several proposals have been made as to the origin of the disagreement for Ar. An early suggestion[10] was that the disagreement could be due to difficulties in measuring the PES values. At this time, the continuum contribution predicted by Smid and Hansen[5] had been found in the new $(e,2e)$ measurements, and if this contribution had provided an unrecognized background in the PES measurements of Spears, Fischbeck, and Carlson[1] the high-energy PES results might be inaccurate. Recently, two other attempts have been made to remove the disagreement; one is the theoretical investigation by Amusia and Kheifets,[11] the other is the experimental investigation by Brion and Tan[9] and Brion, Tan, and Bancroft.[12] However, these attempts yield different answers to the problem. Amusia and Kheifets ascribe the differences between photon- and electron-impact experiments to a difference in the effects of correlation in the two cases. For photoionization, initial-state configuration interaction (ISCI) as well as final-ionic-state configuration interaction is important while for $(e,2e)$, at zero momentum transfer, Amusia and Kheifets found that ISCI can be neglected. As a consequence, they derive for the relative satellite line intensities at high impact energies different values. Contrary to this, in the experimental investigation by Brion, Tan, and Bancroft[12] it is claimed that the intensity ratio $R=I(3d$ satellite$)/I(3s)$ increases with photon energy from the low photon-energy value at 77 eV photon energy (0.17, Ref. 2) towards the value 0.32 given by $(e,2e)$.[7] The increase with photon energy is contrary to the prediction by Smid and Hansen[13] and was taken to indicate that the calculations by Smid and Hansen[5] and by Dyall and Larkins[14] were inaccurate.

In a preliminary study[15] of the satellite spectrum of argon due to photoionization in the 3s and 3p shells, we have demonstrated the capability of our experimental setup for achieving photoelectron spectra of high quality with respect to line separation, background determination, and counting statistics. This capability prompted us to make a detailed experimental investigation of the argon satellite spectrum at high resolution as a function of photon energy.

The experiment was performed at the Berlin electron storage ring BESSY by use of a toroidal grating monochromator (TGM4). Spectra have been taken between 77- and 120-eV photon energy. A special effort was

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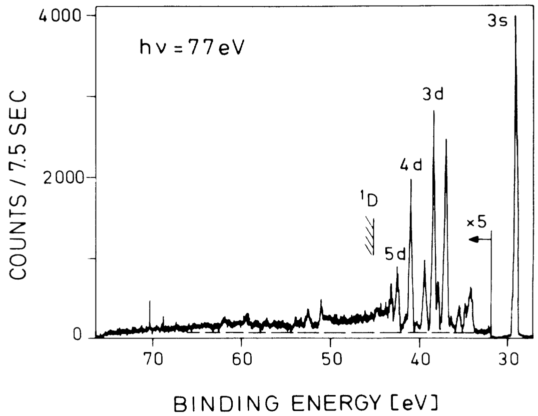

FIG. 1. Spectrum of ejected electrons in argon up to the $3s$ photoline measured at the quasimagic angle. The dashed line indicates our setting of the background.

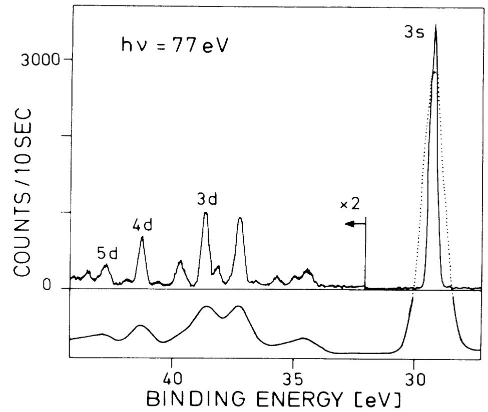

FIG. 2. Satellite lines of argon measured at the quasimagic angle. Upper part: Experimental spectrum obtained in this work. Lower part: Same spectrum convoluted by a Gaussian distribution with 1 eV FWHM.

made at the highest available photon energy of 120 eV where the largest disagreement with theory[13] was found in the previous experiment.[9,12] At this energy the monochromator slits were narrowed to 0.1 mm which resulted in a band pass of about 0.3 eV. Photoelectrons from the interaction region were energy analyzed with a rotatable double-sector cylindrical-mirror analyzer (for details see Derenbach and Schmidt[16]). The instrumental resolution of the analyzers was approximately 0.4%. As discussed by Schmidt,[15] several requirements have to be fulfilled in order to extract the correct relative line intensities from the experimental photoelectron spectra. In the present work these requirements were met.

Figure 1 shows as an example the photoelectron spectrum of argon from threshold up to the $3s$ photoline under excitation by 77-eV photons. The $3s$ photoline as well as the clearly visible nd satellite lines with their ^1D double-ionization threshold are indicated. Many of the satellites are due to $3p$ ionization and are not discussed here.[15] Below the double-ionization continuum some weak features are visible. They are caused by double photoprocesses like $3s$ ionization and excitation of a $3p$ electron to a higher orbital or to the continuum as well as by nonradiative decay of such states. They are not considered further here. From the spectrum it is clear that a constant background correction (determined between the $3s$ main line and the first satellite lines) is appropriate.

Here we will concentrate on the $3d$ satellite line at 38.59-eV binding energy. Figure 2 shows an extended view around this satellite line. The upper part shows the experimental spectrum, the lower part the same spectrum convoluted with a Gaussian of 1 eV FWHM. This convoluted spectrum has a net resolution which is approximately equal to or better than that obtained in the earlier experimental investigations.[1,2,9,12,17] Figure 2 clearly demonstrates two important problems for the evaluation of the $3d$ satellite intensity; correct setting of the background and correct separation of the $3d$ photoline from neighboring features. We find, at 77 eV photon energy, that $R = (17.2 \pm 0.6)\%$. This value is slightly smaller than the value of 19% obtained by Adam, Morin, and Wendin[17] at lower resolution. In order to demonstrate the quality of our data, Fig. 3 shows the satellite spectrum at 120 eV. For this energy the analysis of the data gives $R = (15.4 \pm 0.6)\%$. This value—and to a lesser extent also the values at lower photon energy —strongly contradicts the result of Refs. 9 and 12 that, at 120 eV, report $(26.0 \pm 3.0)\%$. If we *add* the intensity of the two neighboring lines to the $3d$ intensity we get $(25.0 \pm 1.0)\%$, a result capable of explaining the high value of Brion and Tan[9] and Brion, Tan, and Bancroft.[12]

In our work we have found that R is independent of the angle of observation in the plane perpendicular to the

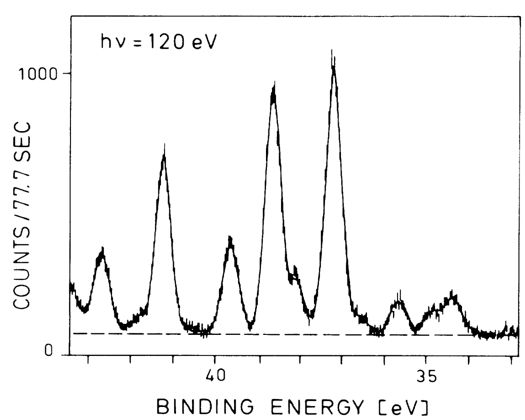

FIG. 3. Satellite lines of argon measured at the quasimagic angle. Experimental data: Points with error bars. Solid line: Least-squares fit to the data. Dashed line: Background.

TABLE I. Satellite intensities measured in the present work at five photon energies relative to the 3s photoline, which is normalized to 100. Also theoretical values for the $nd\ ^2S$ lines are shown evaluated from Ref. 13.

E_b		Energy (eV)	77		90		100		110		120	
(eV)	Label[a]	Limit	Obs.	Theory	Obs.	Theory	Obs.	Theory	Obs.	Theory	Obs.	Theory
34.30	$3d\ ^2F$	^3P	4.1(6)		4.4(6)		3.5(6)		3.6(6)		2.4(4)	
34.86	$3d\ ^2G$	^1D	2.5(6)		2.2(6)		1.4(6)		1.1(6)		1.4(4)	
35.60	$4p\ ^2P$	^3P	2.3(6)		2.5(6)		2.7(6)		2.5(6)		2.1(4)	
36.52	$4s\ ^2S$	^1S	1.1(6)		1.0(7)		0.9(8)		0.4(9)		1.0(6)	
37.13	$4p\ ^2P, 3d\ ^2D$	^1D	18.6(6)		20.0(8)		17.9(8)		19.0(8)		17.3(6)	
38.03	$3d\ ^2D$	^1S	4.3(6)		3.8(8)		3.4(8)		2.9(8)		3.3(6)	
38.59	$3d\ ^2S$	^1D	17.2(6)	17.3	17.0(8)	16.8	16.6(8)	16.6	16.1(8)	16.5	15.4(6)	16.4
39.53	$4p\ ^2P$	^1S	6.9(6)		7.7(8)		6.9(8)		7.0(8)		6.3(6)	
41.20	$4d\ ^2S$	^1D	11.9(6)	9.5	11.4(8)	9.2	11.3(8)	9.0	11.7(8)	9.0	11.2(6)	9.0
41.77			1.1(6)		1.2(7)		0.9(8)		0.5(9)		0.9(6)	
42.64	$5d\ ^2S$	^1D	6.0(6)	5.4	6.6(8)	5.2	5.8(8)	5.1	6.4(8)	5.1	5.4(6)	5.1
43.42	$6d\ ^2S$	^1D	3.5(8)	3.4	4.4(10)	3.2	3.8(10)	3.2	3.7(10)	3.2	3.3(8)	3.1
	$7d-\infty d$[b]	^1D	7(2)	8.6								
	Continuum[b,c]	^1D	33(10)	>27[d]								

[a]See Ref. 15.
[b]Possible contributions from continua based on the ^3P and ^1S thresholds are included.
[c]The continuum contribution from $\epsilon d\ ^2S$ is estimated after subtraction of the discrete features below the double-ionization threshold (Fig. 1).
[d]The intensity shown is the contribution from the $\epsilon d\ ^2S$ continuum at infinite photon energy according to Ref. 5. According to Ref. 13, the real intensity is larger but it is doubtful whether the procedure used to calculate the satellite intensities in Ref. 13 can be used down to very small electron energies.

incoming beam at 120 eV, which implies an angular asymmetry factor β equal to 2. The investigation by Adam, Morin, and Wendin[17] gives, for photon energies up to 70 eV, an angular asymmetry factor of 2 for both lines. It seems unlikely that β will change at still higher energies. This means that the work of Spears, Fischbeck, and Carlson,[1] which was performed with use of the characteristic x-ray radiation (Mg $K\alpha$, Al $K\alpha$), is unaffected by the fact that it was not performed at the magic angle.

Table I gives our results for all the relative intensities measured for photon energies between 77 and 120 eV. We note that there is very good agreement between the predictions of Smid and Hansen,[13] based on the calculations in Ref. 5, and the observed values for the nd satellites including the estimate of the intensity of the $\epsilon d\ ^2S$ continuum at 77 eV. Only for the 4d satellite is there not agreement within the experimental error limits. We show in Fig. 4 a comparison with the work of Brion, Tan, and Bancroft[12] displayed in the same manner as in that paper. The dotted line shows the prediction of Smid and Hansen[13] and the present experimental points, whose size indicate their error bars, are in perfect agreement with the prediction. The full line is drawn by Brion, Tan, and Bancroft[12] through their data points (crosses) and are extrapolated (dashed) to high photon energy where it agrees with the most recent (e,2e) results[6,7] (solid square) but not with the earlier photoelectron results[1] (lozenges). The new experimental results in conjunction with the theoretical predictions are seen to agree reasonably well with the earlier PES results where we note that the value at 1487 eV very recently has been confirmed by Svensson, Helenelund, and Gelius.[18] This result means that there is agreement between theory and PES results at all energies and that the disagreement persists between theory and (e,2e) spectroscopy, which has been conjectured by Smid and Hansen[5] to be due to difficulties in the interpretation of the (e,2e) data.

Finally we would like to comment on the theoretical calculations of satellites in the Ar photoelectron spectrum. Despite the good agreement obtained between theory[13] and experiment in the 77–120-eV photon-energy range it should be kept in mind that these calculations take only final-ionic-state configuration interaction into account. It is well known that the "Cooper minimum" in the cross section for 3s ionization in Ar is a correlation effect due to coupling between the $3s^{-1}\epsilon p$ and $3p^{-1}\epsilon l$ continua. However, this effect is likely to be most important *below* 70 eV. That initial- and final-state correlation also is important in the energy region *above* 70 eV can be seen from the occurrence of $3d\ ^2L$ satellites with $L>0$ (Table I). These effects are not explicitly included in the calculations reported in Ref. 13 and it is therefore possible that the close agreement obtained for the $nd\ ^2S$ satellites in the present work is to some extent fortuitous. An improved calculation which includes ISCI and continuum coupling is in progress.

In the theoretical treatment of Amusia and Kheifets,[11] PES and (e,2e) experiments give different results at high energy. Even though their results are in reasonable

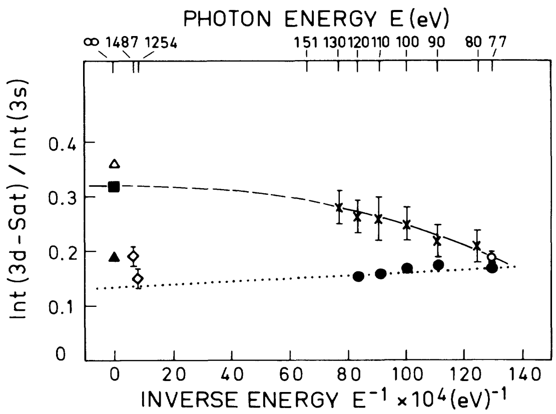

FIG. 4. Intensity ratio $R = I(3d \text{ satellite})/I(3s)$ as a function of inverse photon energy as plotted by Brion, Tan, and Bancroft in Ref. 12. Experimental, PES data (closed circles). This work, the error bars are within the symbols. Lozenges, Spears, Fischbeck, and Carlson, Ref. 1. Open circle, Adam, Morin, and Wendin, Ref. 17. Crosses, Brion, Tan, and Bancroft, Ref. 12. Squares, $(e,2e)$ data from Refs. 6 and 7. Theoretical data, dotted line, Smid and Hansen, Ref. 13. Open triangles, $(e,2e)$ value from Amusia and Kheifets, Ref. 11. Closed triangles, PES value from Ref. 11. The dashed line represents the matching between PES and $(e,2e)$ values proposed by Brion, Tan, and Bancroft in Ref. 12, which is not confirmed in our work.

agreement with the experimental data, in our view a number of problems exist with this theory. For example, the new $(e,2e)$ experiments[8,9] for Xe are in reasonable agreement with the high-energy PES results.[19] In addition, we find for Ar that β is equal to 2 up to at least 120 eV. This is unlikely if Amusia and Kheifets's theory is correct since the large difference between $(e,2e)$ and PES in that theory is based on the influence of configuration interaction in the initial state on the photoionization cross sections. If ISCI is as strong as calculated by Amusia and Kheifets it is most likely also to have an effect on β. Finally, the calculations of $3s3p^6$ amplitudes in Ar II differ between Amusia and Kheifets, on the one hand, and Smid and Hansen[5] or Dyall and Larkins[14] on the other. This is puzzling since the same physical effects seem to be included in the calculations.

In conclusion, we have shown the utmost importance of having adequate resolution in PES of satellite spectra. The existence of $3p$ satellites in the same energy region as the $3s$ satellites complicates the measurement of intensities and it perhaps also complicates the $(e,2e)$ measurements where it has been assumed in the past that $3p$ satellites can be neglected. We have demonstrated that there is very close agreement in the 70–120-eV energy range between the PES results and the calculations presented in Ref. 13 for the ^2S satellites. However, the presence of a number of satellites of different LS character show that a more sophisticated calculation now is warranted not only in the region of the "Cooper minimum" but also at higher proton energies. Such a calculation is in progress.

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