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LETTER TO THE EDITOR

High-*l* satellite states in the threshold photoelectron spectrum of argon

Bertold Krässig[†]||, Jørgen E Hansen[‡], Willy Persson[§] and Volker Schmidt[†]

† Fakultät für Physik, Universität Freiburg, D-79104 Freiburg, Germany

‡ Van der Waals-Zeeman Institute, University of Amsterdam, Valckenierstraat 65,

NL-1018 XE Amsterdam, The Netherlands

§ Department of Physics, Lund Institute of Technology, S-221 00 Lund, Sweden

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Abstract. An interpretation is given of the threshold photoelectron spectrum of Ar between the ³P and ¹D double-ionization thresholds. In this region the observed spectrum is less cluttered than below the ³P thresholds and the interpretation is more straightforward. One of the characteristic features of the spectrum is the excitation to Rydberg orbitals with high angular momentum *l* in agreement with the Wannier picture as first discussed by Fano in 1974.

Threshold photoelectron spectroscopy of atoms has turned out to be a very convenient way of obtaining information about excited states above the first ionization threshold. The attainable energy resolution is superior to that in other electron spectroscopies with the consequence that the uncertainty in the determination of the energy of the excited state is considerably reduced. In this way it is possible to confirm excited states which have been observed in other spectroscopies, but, more importantly, new levels can also be established. Firstly, because at threshold different population mechanisms are at work, and secondly, because states which lie above ionization limits are often difficult to detect in other ways, e.g. in emission spectroscopic information. However, the interpretation of such a spectrum is often complicated, since both single- and double-excitation thresholds can be observed and the only good quantum numbers are those implied by the dipole character of the excitation. This may lead to a very cluttered spectrum since a large number of ionic states can couple to the required total angular momentum.

It was pointed out by Fano (1974) that the Wannier theory (Wannier 1953) implies that, at energies close to the ionization threshold, exchange of angular momentum becomes possible between the incident and the excited electron in an electron–atom collision or, analogously, between two excited electrons in a double photo-excitation. As a consequence, high angular momentum states can be populated. This prediction has been generally accepted and a number of later theoretical studies have supported the idea (Drukarev 1982, Rau 1984, Read 1984). Also some experimental studies have been reported in which the population of high-*l* states near the ionization threshold has been observed in electron-impact experiments (Tarr *et al* 1981, Hammond *et al* 1984, 1988) and in threshold photoionization (Hall *et al* 1991).

|| Present Address: Physics Division, Argonne National Laboratory, Argonne IL 60439, USA.

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We report here on a case which, due to fortunate circumstances, shows in a particularly clear-cut manner the importance of high-*l* Rydberg states in photo-excited threshold electron spectra as predicted on the basis of the Wannier theory. Specifically we discuss in this letter the threshold photoelectron spectrum of neutral Ar between the $3p^4({}^{3}P)$ and $({}^{1}D)$ double-ionization limits where most of the possible excited Ar⁺ states are of the type $3p^4({}^{1}D)nl$. Very few of these states are known. This is because most states in this region are autoionizing and such states are difficult to establish in emission spectroscopy which is the main source of information about the level structure of Ar II, primarily through the work of Minnhagen (1963), although some levels have been added later. We note, in particular, the study of levels with high *l* values by Quinet *et al* (1994).

The threshold photoelectron spectrum of Ar has been studied previously by Becker *et al* (1988), Hall *et al* (1989, 1992a, c), Wills *et al* (1989), Heiser *et al* (1992) and Cvejanović *et al* (1994), and the published spectra demonstrate the rapid development of the experimental techniques during the last 10 years. However, in none of these works has a detailed interpretation been attempted of the spectrum above the ³P threshold at 43.4 eV excitation energy. Hall *et al* reported that 'Rydberg states can clearly be seen converging to the ¹D limit where a well defined cusp is visible'. In contrast, Cvejanović *et al* concluded, presumably on the basis of the asymmetry of the dip observed at threshold, that 'a higher resolution investigation of the region...should reveal structure due to neutral resonances—rather than due to (¹D)*nl* satellite states'. We discuss here a new measurement of the spectrum in the range 41–45.6 eV, concentrating primarily on the region between the ³P and ¹D thresholds. The spectrum is shown in the upper part of figure 1.

The spectrum has been obtained at the electron storage ring BESSY in Berlin, using the monochromator TGM4 and an improved version of the ZEKE (zero kinetic energy) analyser described by Krässig and Schmidt (1992). In short, this analyser employs a pulsed electric field which is suitably synchronized and delayed with respect to the short flash of light from the electron storage ring operated in single-bunch mode. By choosing a shorter or longer pulse delay, the upper limit for the kinetic energy of the electrons collected from the source region can be modified. An important improvement to the set-up described by Krässig and Schmidt (1992) is that a set of 40 mm diameter multi-channel plates has been used as a detector. This improved both the time resolution in the time-of-flight measurement and the efficiency of threshold electron detection. The spectrum in figure 1 was obtained using a 1 V cm⁻¹ extraction pulse with a delay of 45 ns resulting in an analyser resolution of roughly 40 meV FWHM. This gave a good match to the energy resolution of the TGM4 monochromator in the region of interest, approximately 45 meV at 45 eV photon energy with 50 μ m slits. The high collection efficiency of the analyser permitted us to record the spectrum with less than 1.5% statistical error in a single scan and 10 s dwell time per point. (The necessity to add individually scanned spectra in order to improve the statistics is probably the reason that the spectrum published by Cvejanović et al (1994) shows less structure than figure 1, although the resolution quoted by Cvejanović et al, 25 meV at 33 eV, is better than ours, see above.) For the spectrum in figure 1 the step size in the scan was 10 meV in the 41-45 eV energy range and 50 meV beyond 45 eV photon energy. The relative uncertainty of energy intervals in our spectrum is less than $\pm 0.2\%$. Due to the absence of an isolated structure with a well known energy in this energy range, the calibration of our energy scale had to rely on auxiliary measurements of which the uncertainty is about ± 20 meV. A comparison of our spectrum in its entirety with the optical data from Minnhagen (1963), however, leads us to conclude that the absolute error in the given energy positions is likely to be closer to half this amount. The spectrum has been normalized to constant photon flux. The estimated background level in the spectrum



Figure 1. The ZEKE spectrum of Ar between 41 and 45.6 eV photon energy obtained as described in the text. The data taking time for this spectrum was about 70 minutes. The positions of the $3p^4$ 3P_J and 1D double-ionization thresholds are marked above the spectrum. Light vertical lines leading to full circles below the spectrum depict the positions of observed levels (mostly Minnhagen 1963); lines leading to open squares signify positions of levels arising from extrapolations described in the text. Assignments can be obtained when following the dotted horizontal lines to the respective labels on the left. The bold vertical bars at the bottom of the figure represent the positions of resonances due to double excitations as reported by Madden *et al* (1969).

is indicated in the figure by the broken curve. The target pressure in the source region of the analyser was about 0.2 Pa.

The spectrum in figure 1 is seen to be rich in detail below the ³P thresholds. In this region the spectrum can be compared with the observations from emission spectroscopy and such comparisons have been published already (Hall *et al* 1989, Heiser 1992, Cvejanović *et al* 1994). The vertical lines below the spectrum leading to full circles in the lower part in figure 1 show the positions of the observed and assigned Ar II levels in this energy region (primarily Minnhagen 1963). Good agreement is obtained between the threshold electron spectrum and an interpretation based on the known optical levels (Hansen *et al* 1996). In the past the necessity to include quartet states in the interpretation has been mentioned in several publications. While a discussion of this point is made difficult by the fact that the coupling conditions in Ar II, except for some of the lower terms, are far from *LS*, we note that our interpretation of the ZEKE spectrum from 41 eV to the ³P thresholds does not require the introduction of genuine quartet states. A similar conclusion has been reached by Lundqvist *et al* (1994) in a high-resolution study of the photoelectron spectrum at 40.8 eV using monochromatized He II light.

Turning to the region above the ³P threshold, which has received scant attention in

the past, it can be seen in figure 1 that this part of the spectrum is considerably cleaner. The figure clearly exhibits the existence of a Rydberg series converging on the ¹D limit (peaks 20, 22, 23–27 in figure 1). It is remarkable that the observed lines, although known to autoionize (Hall et al 1992a), are sharp and show no broadening that could be attributed to PCI. In fact, the width of these peaks is smaller than what would be expected from the combined monochromator/spectrometer resolution and nearly matches the pure monochromator bandwidth. This can be explained by a sharp drop in the excitation cross section of these states at threshold across the energy interval spanned by the analyser response function. The inference is that these satellite states are preferentially excited very close to threshold. In an attempt to interpret this part of the spectrum, the Rydberg series built on the $3p^4({}^1D)$ parent have been extrapolated using the known $({}^3P)nl$ and $({}^1D)nl$ level values (Minnhagen 1963), the Ar III ³P-¹D separation (Minnhagen 1960) and quantum defect considerations. The levels obtained are indicated as open squares in the lower part of figure 1. Among the Rydberg series, the $3p^4({}^1D)nd {}^2S$ series (identified up to n = 9by Krause et al 1992) is well known to dominate the satellite structure at higher photon energies (Kossmann et al 1987, Svensson et al 1987, Krause et al 1992) due to its close association with the ionization of a 3s electron in Ar. In the threshold spectrum in figure 1, however, this series matches neither the absolute positions nor the relative spacings of the pronounced Rydberg structure between the ${}^{3}P$ and ${}^{1}D$ limits. The suppression of the nd 2 S series is in agreement with theoretical work (Wijesundera and Kelly 1989, Sukhorukov et al 1992) that predict a minimum for the satellite strength in this region of photon energy. Also the extrapolations of the $(^{1}D)ns$ and np series point only to very weak structures in figure 1. In contrast, the predictions for the nf and ng series with principal quantum numbers n = 6-12 give excellent agreement with the observed peak structure.

The figure also shows that the proposed assignment is supported by a reasonable degree of continuity across the ³P ionization threshold when comparing with the intensity of the 4f and 5f/5g peaks (labelled 4, 5 and 15 in figure 1) below the threshold, even though the latter structures are partly mixed with others and an estimate of the intensity is more difficult than for the higher levels. The low levels demonstrate, however, the extent of the finestructure splitting of the (¹D)nf subconfiguration which becomes smaller with increasing n and cannot be resolved for the higher n values. The extrapolated levels for n f and ng are therefore based on the centre of gravity of the respective splittings. Furthermore, the *n*f and *n*g series are barely separated from each other for n = 5, while for n = 6 their separation causes just a slight asymmetry in the observed peak (peak 20 in figure 1) which is beyond the instrumental resolution at higher n. In fact, due to the nearly hydrogenic nature of the Rydberg series with l > 2 in the Ar II spectrum, we expect that all the high-l Rydberg series will overlap, while the ns, np and nd series members will be separated at least for n < 10 with the present resolution. Thus the fortunate circumstances, which have produced a very clean spectrum in this case, allow us to interpret the spectrum as showing two types of Rydberg series: the non-hydrogenic ns, np and nd series, which are separated from each other, and the higher-*l* series that are hydrogenic and thus overlap each other. The spectrum shows that the ns, np and nd Rydberg series converging on the ¹D threshold have virtually died off for n > 7, while the series corresponding to nf, ng and probably higher l retain their significance to much higher n values. Table 1 gives the calculated values of the centres of gravity for the members of the $(^{1}D)nf$ and ng series with n = 6-12together with the observed peak positions and the identification number used in figure 1. The estimates in table 1 are based on the already mentioned ingredients; the observed levels, the known ${}^{3}P^{-1}D$ limit separation and the variation with *n* of the quantum defects for f and g series (Edlén 1964, Persson and Valind 1972). In order to use all available data for

Table 1. Observed and calculated energies (in eV, measured relative to the Ar I ground state) of the features in figure 1 between the ³P and ¹D limits and the centre-of-gravity energy values of the (¹D)nf and ng series members, respectively.

			Calculated energies ^a			
Observed features		nf series		ng series		
label ^b	energy ^c	n	energy	п	energy	
20	43.613	6	43.596	6	43.612	
22	44.009	7	44.003	7	44.014	
23	44.264	8	44.268	8	44.275	
24	44.445	9	44.449	9	44.454	
25	44.575	10	44.578	10	44.582	
26	44.665	11	44.674	11	44.676	
27	44.735	12	44.746	12	44.748	

^a Estimated uncertainty: better than 1 meV.

^b Refers to the identification label in figure 1.

^c Estimated uncertainty: 10 meV (see the text).

the extrapolation, the splitting of the $({}^{2S+1}L)nl$ subconfigurations as a function of *n* was studied. This made it possible to also determine the centre of gravity of a subconfiguration accurately in cases where only a few of the levels involved are known.

An explanation for the observations can be obtained via the Wannier theory (Wannier 1953). In the typical situation close to the ionization threshold treated in this theory, two electrons become closely correlated as they move away from the residual ion core with low velocities. Fano (1974) pointed out that the low velocity of the electrons enables them to exchange angular momentum in an amount sufficient to attain high *l* values. If the energy deposited is insufficient to lift both electrons into the continuum, only one of the electrons actually escapes, but the *l* value of the other (bound) electron will nevertheless reflect this distribution. Thus we expect the ZEKE spectrum to show a distribution of *l* values for the excited electron with increasingly higher *l* values when going to larger values of *n*. This is precisely what we see in figure 1 where the high-*l* peaks are the dominant features as the ¹D limit is approached. It is worthwhile noting that the corresponding high-*l* series converging to the ³P_J limits are also present and can be identified in figure 1 up to n = 8.

Several authors have tried to put this idea on a more quantitative footing (Drukarev 1982, Rau 1984, Read 1984) and have given formulae for the population distribution over l as a function of principal quantum number n of the excited electron. If we apply the formula from Drukarev (1982) to the n = 7 manifold, for example, we find a distribution peaked between l = 1 and l = 2 and an intensity of the d peak structure which should be roughly equal to the intensity of the combined high-l peak. Compared to figure 1, this prediction seems to underestimate the intensity of the high-l peak. The same conclusion holds for the model calculation of Rau (1984) which predicts an even smaller relative intensity for the high-l peak. We note that Hammond *et al* (1988) reported the same systematic disagreement in the related case of electron-impact threshold excitation of the Kr and Xe $({}^2P_{1/2})nl$ states. Thus it looks as if the idea that high-l states are populated at threshold is essentially correct, but that the quantitative treatment needs to be improved.

We note that the present case does differ in many aspects from the situation discussed in the cited theoretical treatments and that many of the assumptions used therein may not be fulfilled here; (i) unlike the case in hydrogen or helium, where the energy separation for a given n, particularly between the low-l Rydberg states, is considerable, e.g. the separation in energy 7s–7f is nearly as large as the separation between the 7f state and the ¹D limit. As the Wannier prediction is believed to apply only within a certain range from the double ionization threshold, the low-*l* states may not be treated on the same footing as the nearly hydrogen-like high-*l* states. (ii) Following photo-excitation the total angular momentum of the two-electron complex in conjunction with a ¹D ionic core can be ¹P, ¹D or ¹F which allow for many more combinations l_1, l_2 of the individual electrons than in the ¹S case studied in the theoretical predictions. Also, the fact that the excited electrons in our case stem from p rather than from s orbitals may influence the distribution of *l* values observed. (iii) Another problem is that particular population mechanisms, which are also effective far from threshold, might skew the distribution away from the Wannier prediction. An example is the series of terms (¹D)*n*d ²S, mentioned above, which are populated via the 3s excitation as is well known from results using higher photon energies (Kossmann *et al* 1987, Svensson *et al* 1987, Krause *et al* 1992); due to a minimum in the cross section the population of these particular satellites is suppressed in the region of interest.

A very interesting question concerns the intensity distribution over the series, in particular, as the ¹D threshold is approached. Inspection of figure 1 shows an intensity distribution with a regular decrease in the intensity of the high-*l* series with *n* followed by an increase in intensity when the series members can no longer be resolved and then a decrease to the ¹D threshold. It is conceivable, though, that the increase in threshold electron intensity just below 45 eV is additionally enhanced due to interference from a resonant structure which has been observed near 44.8 eV in the photo-absorption experiments of Madden *et al* (1969). The bold vertical lines at the bottom of figure 1 indicate the positions of the doubly-excited resonances observed in these measurements. In principle every satellite state forms the limit for a series of doubly-excited states. The region just below the double-ionization threshold therefore contains a high density of (possibly weak) doubly-excited resonances. These neutral resonances generally have a propensity to autoionize to the nearest ionic Rydberg state (Niehaus 1988, Hansen 1989, Rost and Briggs 1991) with the consequence that a low-energy electron is emitted that enhances the signal of ZEKE electrons.

Another consequence of applying the ideas of Wannier theory to the energy regime on both sides of the threshold is that the energy dependence of the threshold electron emission should display a cusp-like structure at the energy of the threshold. An analysis of this effect for the case of single ionization by electron impact (Read 1984) predicts the wings on both sides of this cusp to be nearly symmetric (cf Cvejanović et al 1995). Such a cusp-like structure seems to be obscured or too weak to be observable in our spectrum at the doubleionization thresholds in figure 1. We note, as did Cvejanović *et al* (1994), that at the ${}^{1}D$ threshold the decrease of satellite intensity below threshold is not symmetrically matched by an increase in threshold electron intensity from double ionization above threshold. In contrast, at the ${}^{3}P_{J}$ limits, in spite of superimposed satellites converging to higher limits, one notices that the continuous level of ZEKE electrons between peaks is clearly higher above threshold than below. However, strong evidence exists (Krässig 1994) that this increase in ZEKE intensity is not just to be attributed to electrons from direct double ionization. There is also a significant contribution of low-energy autoionization electrons from the decay of the satellite states associated with the peak structure labelled 18 in figure 1 to the ${}^{3}P_{2}$ final state (cf Hayaishi et al 1988, Hall et al 1992b, Krässig and Schmidt 1992). As a further complication for a quantitative analysis of the cusp region, the possibility of a modification of the population distribution through collisional effects in the target gas has to be considered (cf Reddish and Cvejanović 1995, Cvejanović et al 1995).

In conclusion we believe that we have found a case that shows, in a particularly straightforward manner, the importance of the high-*l* states in ZEKE spectroscopy caused

by the low-energy electrons involved. While there is qualitative agreement with published theoretical discussions, more work, both theoretical and experimental, must be performed before quantitative agreement is obtained.

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