

## Photoelectron satellite spectrum in the region of the 3s Cooper minimum of argon

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The 3s,3p satellite spectrum of argon has been studied with use of synchrotron radiation in the 40–70-eV energy range. In the region of the 3s Cooper minimum ( $42.5 \text{ eV} \pm 0.2$ ), the integral intensity of the satellites is ten times larger than the 3s partial cross section. The angular asymmetry parameters have been measured as a function of the photoelectron energy for the  $3s^2S, 3p^2P$  final states as well as for the satellites. For the lowest photon energies it appears that the  $\beta$  parameter values of the most intense satellites are strongly dependent on the total angular momentum of the final ionic state.

### I. INTRODUCTION

Photoelectron spectrometry is a powerful tool for studying electron correlation effects. When a single electron is removed from a single subshell through photoionization some excited states of the ion may be observed directly by the presence of satellite lines on the low kinetic-energy side of the main lines (ionic ground states) in the corresponding photoelectron spectrum.<sup>1,2</sup> For argon, krypton, and xenon, experiments<sup>3,4</sup> were carried out using x-ray emission lines: 1487, 1254, and 151 eV. At these energies the assignments of strong satellite structures have been based on configuration-interaction calculations involving the  $ns^1np^6^2S$  and  $ns^2np^4n'l'^2S$  final states of the ions.

Recently Adam *et al.* and Fahlman *et al.* studied these satellites in xenon,<sup>5,6</sup> and in argon<sup>7</sup> using synchrotron radiation in the 33–80-eV photon-energy range, confirming the rich satellite structure above, respectively, the 5s,5p and the 3s,3p ionization thresholds. Süzer *et al.*<sup>8</sup> reported a high-resolution spectrum of some of these satellites in the xenon case, using an HeII radiation at 40.8 eV.

All these data indicate that for the Xe and Ar cases the relative intensities of the various satellites show strong variation when the energy of the incident radiation changes from 33 to 1487 eV. They also show clearly that the satellite spectra resulting from photoionization in the outer shell of argon involve both the 3s and 3p subshells and that the final-ionic-state configuration-interaction (FISCI) mechanism describes only part of the spectrum.

In this paper we present satellite spectra of argon whose

binding energies vary from 32 to 43 eV, using synchrotron radiation in the 40–70-eV photon-energy range. We have measured angular asymmetry parameters for all the resolved satellites.

We have recorded satellite spectra much better resolved than those previously obtained.<sup>7</sup> Moreover, measurements of angular distributions made it possible to observe new satellite lines, as will be shown later. The present work and the work of Fahlman *et al.*<sup>6</sup> concern the intensities of satellite spectra at photon energies where the intensities of the main s line (3s in argon, 5s in xenon<sup>6(b)</sup>) goes through a minimum. The study of satellite structure in argon is more tractable because obscuring Auger lines are absent, which made the interpretation of the xenon spectra difficult.

### II. EXPERIMENT AND RESULTS

The experiments were carried out with a 127° cylindrical analyzer using the synchrotron radiation emitted by the ACO storage ring (les Anneaux de Collisions de l'Accélérateur linéaire d'Orsay) and a grazing incidence monochromator.<sup>9,10</sup> The two gratings used to perform this experiment were blazed in order to get a maximum of diffracted light at 250 Å (1800 g/mm) and at 150 Å (2400 g/mm). The band pass of the monochromator was set, respectively, at 1.7 and 1.2 Å. The analyzer was operated in a constant pass-energy mode ( $E_a = 10 \text{ eV}$ ) with a resolution of 7%. The electrons were detected by a channeltron; a coincidence technique taking into account the pulse

TABLE I. Experimental binding energies of satellites 1-6 and angular anisotropy parameter for various energies in the 40 eV up to 70 eV energy range.

|                   | Binding energy (eV) and anisotropy parameter |                                | Photon energy (eV) |                  |                   |                     |                   |                   |                       |
|-------------------|--|--------------------------------|--------------------|------------------|-------------------|---------------------|-------------------|-------------------|-----------------------|
|                   | Spears <i>et al.</i><br>(Ref. 3)             | Adam <i>et al.</i><br>(Ref. 7) | This work          | 40               | 43                | 45                  | 55                | 62                | 70                    |
| $3p^2P_{3/2,1/2}$ |  | 15.82 <sup>a</sup>             | 15.82 <sup>a</sup> | 1.6 <sup>b</sup> | 1.05 <sup>b</sup> | 0.72 <sup>b</sup>   | 0.25 <sup>b</sup> | 0.38 <sup>b</sup> | 0.85 <sup>b</sup>     |
| $3s^2S$           | 29.3   | 29.30                          | 29.3               | 2.05(20)         | 1.8(4)            | 2.0(2) <sup>b</sup> | 2.0(15)           | 1.90(15)          | 2.10(15) <sup>b</sup> |
| 1                 |  | 34.46                          | 34.54(10)          | 0.8              | 1.35              | 1.3                 | 0.0               | 0.27              | -0.33                 |
| 2                 |  | 35.37                          | 35.63(8)           | 0.14             | 0.10              | 0.50                | 0.45              | 0.80              | 0.70                  |
| 3                 | 37.4   | 37.27                          | 37.26(7)           | -1               | -0.8              | 0.03                | 0.15              | 0.06              | 0.4                   |
| 4                 | 38.7   | 38.60                          | 38.57(4)           |                  |                   |                     | 2.1               | 2.1               | 2.0(1) <sup>b</sup>   |
| 4'                |  |                                | 39.55(4)           |                  |                   | -0.2                | -1.3              | -0.6              | 0.25                  |
| 5                 |  | 41.22                          | 41.22(4)           |                  |                   |                     | 1.9(2)            | 1.9(2)            | 1.8(2) <sup>b</sup>   |
| 6                 |  | 43.07                          | 42.75(7)           |                  |                   |                     | 2.2(4)            | 2.2(4)            | 1.4(4)                |

<sup>a</sup>The value corresponds to an average between the  $j$  components.

<sup>b</sup>The  $\beta$  values have also been obtained by measuring the intensity variation of the peak for 36 directions around the photon beam.

structure of the ACO light (repetition rate: 73 ns, full width at half maximum: 1.2 ns) permitted the elimination of the major part of the background signal which otherwise may obscure the photoelectron spectra at low kinetic energy. The axis of the cylindrical analyzer was parallel to the photon beam; the analyzer may be rotated from 180° around the incident polarized radiation in order to measure the angular distribution of the detected photoelectrons. The intensity of the photoelectrons ejected at an angle  $\theta$  with respect to the largest polarization vector of the light is given by the following expression:

$$\frac{d\sigma_I(h\nu)}{d\Omega} = \frac{\sigma_I(h\nu)}{4\pi} \left[ 1 + \frac{\beta_I(h\nu)[1 + 3P \cos(2\theta)]}{4} \right],$$

where  $d\sigma_I/d\Omega$  and  $\sigma_I$  are, respectively, the differential and partial cross sections for a given ionization process,  $\beta_I(h\nu)$  is the asymmetry parameter, and  $P$  is the degree polarization. It has been also shown in the literature that for this configuration there exists an angle ["pseudomagic" angle:  $\theta = \frac{1}{2} \arctan(-1/3P)$ ] which makes the number of accepted photoelectrons proportional to the partial cross section.

For all the data presented here the target gas pressure was maintained as low as possible (less than  $5.10^{-5}$  Torr in the volume of the electron spectrometer); no pressure correction was made, and it should be noted that elastic and inelastic electron scattering are expected to be slowly varying for electron kinetic energies higher than 15 eV.

Relative intensities of the lines have been taken as the

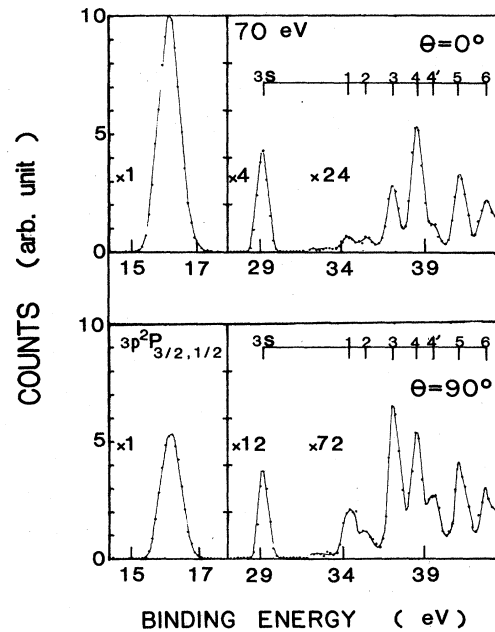


FIG. 1. Photoelectron spectra at 70 eV for two angular positions of the analyzer. Tick marks labeled 1-6 indicate the positions of the satellites identified in this present work (see Tables I and II for the corresponding binding energies and configurations). These spectra are not corrected for the transmission function of the analyzer.

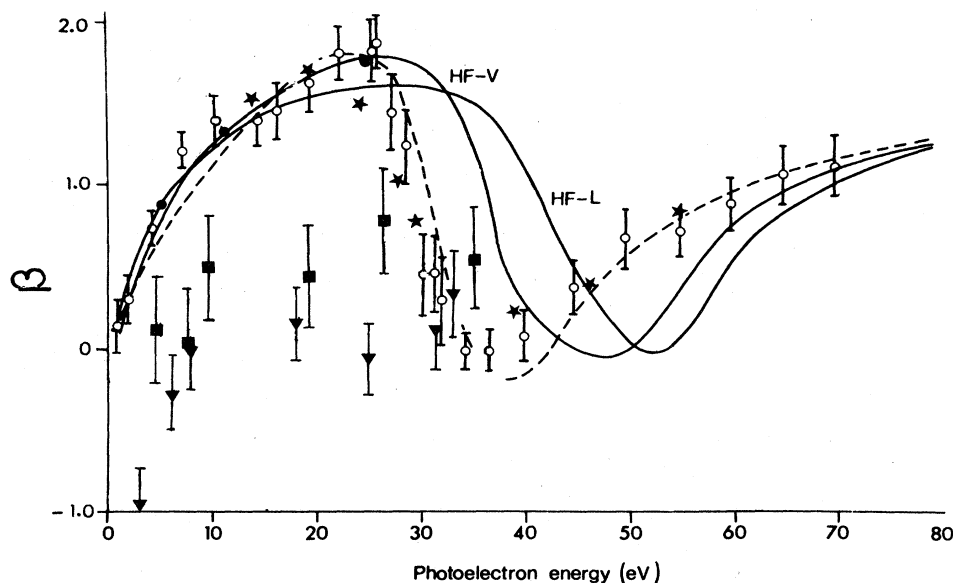


FIG. 2. Asymmetry parameter for the  $3p$  photoelectrons of argon as a function of photon energy.  $\circ$  is Houlgate *et al.* (Ref. 36) (1974);  $\bullet$  is Dehmer *et al.* (Ref. 37) (1975);  $*$  is this work;  $\blacksquare$ ,  $\blacktriangledown$  give the values for satellites respectively labeled 2 and 3. Solid curves are the single-electron Hartree-Fock length and velocity (HF-L and -V) calculations of Kennedy *et al.* (Ref. 38) (1972). The dashed curve is the random-phase approximation with exchange calculation of Amusia *et al.* (Refs. 39 and 40).

relative areas corrected for the variation of the spectrometer transmission with kinetic energies. For each spectrum a Gaussian deconvolution gives the width of the unresolved  $3p^2P_{3/2,1/2}$  and  $3s^2S$  photoelectron lines. This width was then used in order to deconvolute the unresolved satellite spectra and to get the correct relative area.

$\beta$  values are obtained from the ratio of the intensities of a deconvoluted line observed at  $0^\circ$  and  $90^\circ$  from the polarization vector of the light. The degree of polarization  $P$  is

measured for all photon energies by recording the angular distributions of the He( $1s$ ) photoelectron line with a  $\beta$  value of 2.

Figure 1 shows photoelectron spectra of argon obtained with a 70-eV photon energy. Satellite peaks are labeled 1–6, as previously<sup>7</sup> proposed. Figure 2 shows  $\beta$  parameters at various photon energies. The experimental results for the corresponding binding energies and for the asymmetry parameters of the various peaks are summarized in Table I. The intensities of the photoelectron peaks rela-

TABLE II. Intensities of the  $3s, 3p$  and related satellite lines relative to the  $3s$  main line. Error bars on the last significant number of each value are indicated in parenthesis.

| eV             | This work |                      |                      |         |         |         |                 | Previous work    |                   |
|----------------|-----------|----------------------|----------------------|---------|---------|---------|-----------------|------------------|-------------------|
|                | 40        | 43                   | 45                   | 55      | 62      | 70      | 77 <sup>a</sup> | 150 <sup>b</sup> | 1487 <sup>b</sup> |
| $3p^2P$        | 53(10)    | 80(16)               | 19.8(2)              | 5.5(4)  | 5.0(7)  | 5.4(4)  | 5.7(1)          | 5.33             | 1.45(8)           |
| $3s^2S$        | 1         | 1                    | 1                    | 1       | 1       | 1       | 1               | 1                | 1                 |
| 1              | 1.5       | 1.8                  | 0.75                 | 0.46    | 0.15    | 0.09    | 0.06            |                  |                   |
| 2              | 0.89      | 1.27                 | 0.38                 | 0.03    | 0.02    | 0.036   |                 |                  |                   |
| 3 <sup>c</sup> | 0.11      | 0.33                 |                      |         |         |         |                 |                  |                   |
| 3              | 4.08      | 4.9                  | 2.08                 | 0.31    | 0.28(2) | 0.20    | 0.16            | 0.15(3)          | 0.03(2)           |
| 4              |           | 0.08(7) <sup>d</sup> | 0.08(7) <sup>d</sup> | 0.20(2) | 0.20(2) | 0.19(2) | 0.19            | 0.15(2)          | 0.19(2)           |
| 4'             |           | 1.68                 | 0.55                 | 0.07    | 0.08    | 0.07    |                 |                  |                   |
| 5              |           |                      |                      | 0.13(3) | 0.14(3) | 0.13(3) | 0.08(2)         | 0.08(3)          | 0.06(3)           |
| 6              |           |                      |                      | 0.06    | 0.06    | 0.04    |                 |                  |                   |

<sup>a</sup>Adam *et al.* (Ref. 7); at 77 eV, peaks 3 and 4 are not resolved.

<sup>b</sup>Spears *et al.* (Ref. 3).

<sup>c</sup>This peak arises at a binding energy of 36.6 eV.

<sup>d</sup>This value is a tentative evaluation made with a photoelectron spectrum recorded at  $0^\circ$  from the direction of the greatest component, expecting a value equal to 2.

tive to the  $3s^2S$  photoelectron line taken at various photon energies are given in Table II.

### III. DATA ANALYSIS AND DISCUSSION

Compared to the experimental results published by Adam *et al.*,<sup>7</sup> the peaks previously assigned 1, 2, 3, and 4 are completely resolved at all photon energies down to 40 eV. The peak labeled 6 (in Fig. 1) is now clearly evident and a new peak labeled 4' is observed which had not been reported before because of the low resolution of the earlier data. Nevertheless, for photon energies lower than 45 eV the deconvolution treatment shows that new satellites must arise on the low binding-energy sides of lines 1, 2, and 3 (see Fig. 3). The resolution and the statistics of our photoelectron spectra are still too poor to give the exact binding energies, intensities, and anisotropy parameters of all the lines expected in the binding-energy range from 34 up to 36.6 eV.

Some of the assignment of satellites can be made by simple comparison of the binding energies of the photoelectron peaks with the energy position of excited final states in ions known from optical spectroscopy.<sup>11</sup> Such an attempt is proposed for the argon case and the results are summarized in Table III. However, because of the high density of excited final states this comparison is not always straightforward and identification must often remain tentative in the absence of calculations.

The presence of strong configuration mixing  $ns^1np^6$ - $ns^2np^4nd$  in the outer  $s$  shell in argon, krypton, and xenon has been known for a long time.<sup>12-14,6</sup> A number of calculations using *ab initio* or semiempirical configuration-interaction methods and many-body techniques<sup>1,15-19</sup> have been performed to explain binding energies and intensities of satellites lines observed in argon, krypton, and xenon photoelectron spectra. In the case of argon an evaluation is proposed<sup>16,17,19(a)</sup> of the satellite intensities relative to the  $3s^2S$  peak; however these results refer to the sudden approximation and consequently may only be

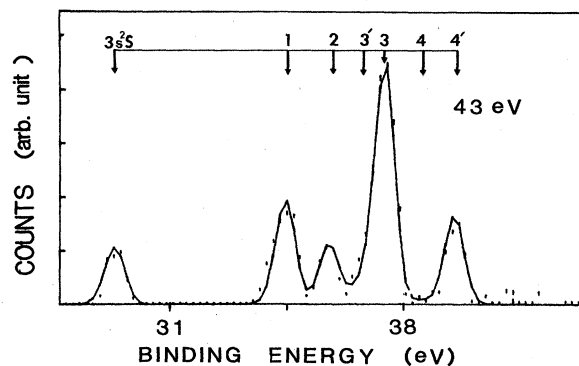


FIG. 3. Photoelectron spectrum recorded at a photon energy of 43 eV and at the pseudomagic angle. Arrows labeled 1-4' indicate the position of the satellites identified in this present work (see Table III). This spectrum is corrected for the transmission function of the analyzer, and the background has been subtracted. Solid curve is a Gaussian fit of the spectrum.

used to interpret photoelectron spectra obtained at the highest excitation energies (i.e., 1487 eV).

The argon satellite spectrum obtained at the intermediate photon energy of 55 eV has a much richer structure than the one observed at 1487 eV. In the absence of available calculations, the assignment of satellites can only be made by comparisons with optical spectroscopy data,<sup>11</sup> absorption measurements,<sup>20</sup> and crude arguments involving variations of relative intensities and anisotropy parameters with excitation energy.

Consequently we shall divide our discussion into three parts: in the first one, Sec. III A, we shall treat the lines 4, 5, and 6 observed at high<sup>3</sup> (and also low<sup>7</sup>) energies, in the second part, Sec. III B, we shall treat lines 1, 2, 3, and 4' which have mostly been observed at excitation energies lower than 70 eV, and in the third part, Sec. III C, we shall discuss the binding-energy spectra around the 36.6-eV energy range.

TABLE III. Relative binding energies of satellites with the  $3s$  main line used as a reference; in the second column the absolute binding energies are deduced from the first column when the  $3s$  main line is given by the optical data (Ref. 11), i.e., 29.235 eV. In the third column we have reported the configurations proposed by the optical data (Ref. 11).

|            | Binding energies<br>(eV) |        | Optical spectroscopy data<br>core: ( $3s^23p^4$ )             |
|------------|--------------------------|--------|---|
| $3s^13p^6$ | 0                        | 29.235 | 29.235  |
| 1          | 5.23(10)                 | 34.475 | $(^3P)3d^2P$ 34.371; $(^3P)3d^2D$ 34.488                      |
| 2          | 6.33(8)                  | 35.565 | $(^3P)4p^2D$ 35.435; $(^3P)4p^2P$ 35.622 <sup>b</sup>         |
| 3'         | 7.35(10)                 | 36.585 | $(^1S)4s^2S$ 36.499 <sup>b</sup>                              |
| 3          | 7.97(7)                  | 37.205 | $(^1D)3d^2D$ 37.183; $(^1D)4p^2D$ 37.253; $(^1D)4p^2P$ 37.107 |
| 4          | 9.27(4)                  | 38.505 | $(^1D)3d^2S$ 38.579 <sup>b</sup>                              |
| 4'         | 10.25(4)                 | 39.485 | $(^3P)5p^2P$ 39.325; $(^3P)5p^2D$ 39.375; $(^3P)4d^2P$ 39.385 |
| 5          | 11.93(4)                 | 41.165 | $(^1D)4d^2S$ 41.202   |
| 6          | 13.45(7)                 | 42.685 |   |

<sup>a</sup>The configurations correspond to final states with binding energies at 0.1 eV from the respective one reported in the second column.

<sup>b</sup>These configurations correspond to the limits of Rydberg series identified in photoabsorption experiments [Madden *et al.* (Ref. 20)].

<sup>c</sup>This line is only observed at the low photon energies (40 and 43 eV).

### A. Lines 4, 5, and 6

#### 1. Partial cross-section measurements

There is agreement between the optical spectroscopy data<sup>11</sup> (Table III) and the calculations<sup>16,19</sup> to assign peaks labeled 4 and 5 to final ionic states of the type  $3s^2 3p^4 nd^2 S$  ( $n$  equal, respectively, to 3 and 4). These two peaks are connected to the  $3s$  hole via the final-ionic-state configuration-interaction (FISCI) mechanism  $3s 3p^6 2S$ ,  $3s^2 3p^4 nl^2 S$ .

*Lines 4 and 5.* Our results show that at 55-eV photon energy the intensity of peak 4 has reached a constant value of 19% relative to the intensity of the main  $3s$  photoline (Table II). An equivalent situation seems to exist in the case of satellite 5 if we take into account the error bars. The absorption experiment<sup>20</sup> carried out through the 20–50-eV energy range gave the total photoionization cross section of argon. In the 30–45-eV energy range this cross section is mostly (more than 80%) equal to the partial photoionization cross section of the  $3p$  subshell. Madden *et al.*<sup>20</sup> have observed autoionization of two-electron excited neutral states. They suggested that some of these states (between 38.07 and 38.42 eV) would be of the type  $3s^2 3p^4 ({}^1D) 3d ({}^2S) np$ ; the limit  $n \rightarrow \infty$  of this Rydberg series is satellite 4 observed in our photoelectron spectrometry experiment.<sup>21</sup> As the oscillator strength is continuous between a Rydberg series and the corresponding continuum, this would imply that the satellite intensity is quite noticeable near its onset. Because of the huge background electron signal in the proximity of zero kinetic energy, it is, however, impossible to verify this assumption and see if the relative intensity still keeps the same constant value of 19% all the way down to threshold; for a discussion of threshold effects see Refs. 22 and 23. In spite of the large error bars, our results recorded for the photon energies in the range of the  $3s$  “Cooper minimum”<sup>21</sup> indicate that the absolute intensity of satellite 4 also goes through a minimum value (see Fig. 3) thereby following the behavior of the  $3s^2 S$  main line.

*Line 6* was previously assigned by Adam *et al.*<sup>7</sup> as  $3s^2 3p^4 5d^2 S$ . This identification was not confirmed by the satellite binding-energy calculations of McCarthy *et al.*,<sup>24</sup> Martin *et al.*,<sup>16</sup> Dyall *et al.*,<sup>17</sup> and Smid *et al.*<sup>18</sup> However these calculations also gave relative intensities for the set of final states  $3s^2 3p^4 nd^2 S$  ( $n=3,4,5,6$ ) completely different from one another. Using the argument that relative intensities must decrease smoothly with  $n$  and in spite of a 1-eV difference between the experimental binding energy of satellites 6 and their calculated  $3s^2 3p^4 5d^2 S$  final state, Smid *et al.*<sup>18</sup> concluded that peak 6 was well assigned as  $({}^1D) 5d^2 S$ .

Smid's conclusion needs a comment: In configuration-interaction (CI) calculations, if the configuration mixing is limited to a few excited states, e.g.,  $3s 3p^6$  and  $3s^2 3p^4 nd$ ,  $n=3,4,5$ , in particular, the  $n=5$  level will then pick up far too much intensity and become pushed to high in binding energy. This problem never arose in the Green's function (CI) calculation of the  $5s$  hole spectrum of xenon by Wendin,<sup>1,5</sup> since the discrete and continuum satellite levels were treated on an equal footing (CI involving discrete and continuum states). As a result, the  $5s$  sa-

tellite intensities decreased in a smooth manner through the discrete region into the satellite continuum.

#### 2. Asymmetry parameter measurements

For the three values of photon energy 55, 62, and 72 eV the  $\beta$  values of these three satellites are equal to 2 within the limit of the error bars (see Table I), showing that these three satellites are most likely reached by the same kind of process, confirming the conclusion of Smid *et al.*<sup>18</sup> Note, however, that there could be overlapping contributions from other satellite levels, which could lead to  $\beta$  values slightly different from 2 (e.g., line 6 at 70-eV photon energy).

For the  $3s^2 S$  main line the experimental data (Table I) do not show, within the error bars, any departure from the constant value of 2. That is expected<sup>25</sup> by a nonrelativistic model for an  $s$  hole in a closed shell.

Since the anisotropy parameter of satellites 4, 5, and 6 is equal to 2 within the errors bars, it means that these final ionic levels also have predominantly  $3s^2 S$  character. This result corroborates the observed similarity of the cross section of the satellites 4, 5, and 6 with the  $\sigma(3s)$ .

### B. Lines 1, 2, 3, and 4'

#### 1. Partial cross-section measurements

In the low binding-energy part of the spectrum, line number 3 is the most intense one; this line is also observed at high photon energy<sup>3</sup> (1487 eV) with an intensity relative to the  $3s^2 S$  final state ten times less than at 55-eV photon energy. Also in the 40–45-eV photon-energy range around the Cooper minimum of the  $3s$  partial cross section, this relative intensity still increases by at least a factor of 15. This fact was not observed by the previous work<sup>7,26</sup> for line 3 but only for lines 1 and 2. The intensity of the satellite 4' relative to the  $3s^2 S$  main line (100%) is even more important (168%) at 43 eV.

At this point some remarks about the experiments may be made.

Firstly, the integral intensity of the satellite spectrum is ten times larger than that of the  $3s^2 S$  main line in the proximity of its Cooper minimum (Fig. 3). Very recently<sup>6(b)</sup> the same experimental observation has been made in the xenon case.

Secondly, in this energy range 99.2% of the integral intensity is shared between satellites 1, 2, 3, and 4' and less than 0.8% by satellites 4, 5, and 6.

Thirdly, the intensity of all the satellites 1, 2, 3, and 4' relative to the  $3p^2 P$  main line drops smoothly by roughly a factor of 3 as the photon energy increases; for example, in the case of satellite 3, its intensity decreases from 7.7% at 40 eV to 3.7% at 70 eV and decreases further to 2% at 1487 eV. This behavior may be compared to the approximately constant relative intensities of satellites 4, 5, and 6 when they are referred to the  $3s^2 S$  main line (see Fig. 4).

For these three reasons, within the frame of an intensity-borrowing model, it seems to be reasonable to connect satellites 1, 2, 3, and 4' with correlation processes occurring in the  $3p$  subshell. The same conclusion was reached by Adam *et al.*<sup>7</sup> concerning the assignment of satellites 1 and 2.

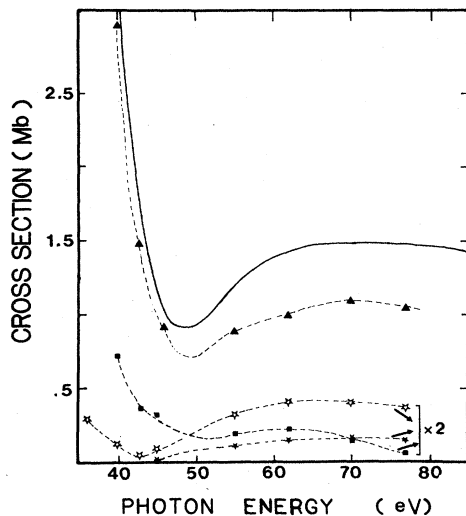


FIG. 4. Total photoionization cross section for argon obtained from the photoabsorption measurements of Marr *et al.* (Ref. 40): full curve. Partial cross sections deduced from the absorption experiments (the double-ionization partial cross section have been taken into account): ▲,  $3p$  cross section; ■, integral intensity for satellites 1, 2, 3, and 4'; ☆,  $3s$  partial cross section; ✱; integral intensity for satellites 4, 5, and 6. Dashed curves are drawn through the experimental points to guide the eye.

## 2. Asymmetry parameter measurements

*Line 3.* From a comparison of the experimental optical data<sup>11</sup> and the Martin *et al.*<sup>15</sup> calculations, Adam *et al.*<sup>7</sup> suggested that for the highest photon energies, peak 3 should arise from the  $3s^2 3p^4(^1D)4s^2S$  configuration, which would involve a FISC process via a  $3s$  hole; for the lower photon energies (77 eV) they suggested that peak 3 should arise from  $3s^2 3p^4 2P, ^2D$  final states.

The variation of the anisotropy parameter with photoelectron energy for satellite 3 (see Table III and Fig. 2) is qualitatively completely different from the variation corresponding to direct ionization of the  $3p$  subshell. It is therefore unlikely<sup>27</sup> that satellite 3 is dominated by the  $3s^2 3p^4 2P$  configuration.

We therefore suggest that peak 3 should mainly be identified with the  $3s^2 3p^4 3d$  configuration [ $3s^2 3p^4(^1D)3d^2D$  level] (see Table III).

Another argument to justify this proposed assignment may be found in the absorption-experiment results of Madden *et al.*;<sup>20</sup> these authors assigned two resonance lines (labeled 85 and 86) as being due to the final states  $3s^2 3p^4(^1D)3dnp$  transitions with  $n$  equal to 8 and 9.

This final ionic state can be reached in three different ways which may all be important in the low-energy region (near threshold) and then explain the high intensity of this line: (i) an ISCI process where initial, virtual,  $3p^6 \rightarrow 3p^4 m d m' d'$  excitations are followed by photoionization of one of the virtually excited electrons, (ii) a FISC process where the photoelectron in a primary (virtual)  $3p \rightarrow \epsilon d$  excitation scatters and creates an additional  $3p \rightarrow 3d$  excitation, (iii) a conjugate shakeup process where

an initial, virtual,  $3p \rightarrow 3d$  excitation is followed by shake-off of another,  $3p$  electron.

*Lines 1, 2, and 4'.* Three identifications have been suggested for the state corresponding to the energy position of satellite 4'. In a recent paper, Dyall *et al.*<sup>19(b)</sup> calculated a possible final ionic state,  $3s^2 3p^4(^3P)5p^2P$ , with a 39.82-eV binding energy, which is 0.5 eV too high if compared with the position of the final state obtained from the optical data (Table III). If we compare the configurations derived from the optical data for the satellites 4' and 2, one may expect that if peak 2 arises from the  $(^3P)4p^2P$  or  $^2D$ , then peak (4') cannot arise from, respectively,  $(^3P)5p^2P$  or  $^2D$ ; there are two reasons for that provided that these two peaks are single states: firstly, the satellite 4' has an intensity twice as high as the peak 2; secondly, the variations of their anisotropy parameters as a function of photoelectron energy are completely different from one another.

Using the same arguments, it is not likely that satellites 1 and 4' may arise from the configurations  $(^3P)3d^2P$  and  $(^3P)4d^2P$ , respectively. A deconvolution treatment of the satellite spectra has shown that unknown satellites exist on the low binding-energy side of lines 1 and 2. Their presence is noticeable only for the lowest photon energy (40–43 eV). Therefore, in our opinion, better resolved satellite spectra are needed in order to interpret the angular anisotropy parameters of satellites 1 and 2, especially if we want to use these  $\beta$  results in order to give clear assignment to these states. For instance, we shall conclude to a  $3p$  parentage of satellites 1, 2, 3, and 4' mainly because of the similarity of the variation of their respective partial cross section with the  $\sigma(3p)$ .

## C. Lines with binding energy around 36.6 eV

One of the most complete Rydberg series of doubly excited neutral states observed by Madden *et al.*<sup>20</sup> concerned the  $3s^2 3p^4(^1S)4s(^2S)np$  ( $n=6-12$ ) excitations. From these authors, the limit would be in agreement with the 36.499-eV binding energy proposed by the optical data<sup>11</sup> but is in conflict with the 37.2-eV binding energy proposed by Ref. 7 and theoretical calculations<sup>15</sup> for satellite 3 assigned as  $3s^2 3p^4(^1S)4s(^2S)$  at high excitation energies. For the low photon energies (40 and 43 eV) we have observed an enhancement on the high kinetic-energy side of satellite 3, which might correspond to a new peak arising at a 36.6-eV binding energy (Table III). However, because of the poor statistics and resolution we cannot tell whether this line vanishes in the x-ray spectra; if it does not disappear then it could be connected with the FISC peak  $3s^2 3p^4(^1S)4s(^2S)$ .

## IV. SUMMARY

In the present case of atomic argon we have considered the photon-energy dependence of the partial photoionization cross sections and the angular asymmetry parameter  $\beta$  for the  $3s$  and  $3p$  main lines and also for a number of satellite lines. An important issue has been whether the intensity of any given satellite shows a photon-energy dependence and an angular dependence similar to that of

the  $3s$  or the  $3p$  main line.

We conclude that the signature of the photoelectron energy dependence of the  $\beta$  factor is clear in the case of the  $3s$ , as well as in the case of three satellites (4, 5, and 6). These satellites can be characterized as  $3s^2 3p^4 nd^2 S$  and clearly share their intensity with the  $3s$  main line with a constant ratio whatever the photon energy.

For all the other satellites (1, 2, 3, and 4'),  $\beta$  lies typically between 0 and 0.5 and from these data we cannot deduce any clear  $3p$  parentage which is only suggested by the similarity in the variation of the partial cross sections. We propose that satellite 3 the most intense, can be characterized as  $3s^2 3p^4 3d$  corresponding to term levels *different from*  $^2S$ . It would derive its intensity from correlations among the  $3p$  electrons in the initial (ground) state [initial-state configuration interaction (ISCI)]. This conclusion is also supported by many-body calculations for argon<sup>28–32</sup> and xenon.<sup>29,33</sup> It has been demonstrated that introduction of initial-state configuration interaction (ISCI, also called ground-state correlation) appreciably affects the variation of the photoionization cross section as a function of photon energy. In the language of configuration interaction this ISCI is obtained by a mixing of the  $np^6 ^1S$  ground state with configurations like  $np^4 m l m' l' (^1S)$ . The dominant part of the  $3p$  partial cross section is given by the  $3p \rightarrow \epsilon d$  transitions and this is the reason why the most important ISCI process is obtained by the interaction of the doubly excited neutral states  $np^4 m d m' d'$  with the  $np (^1S)$  ground state. This type of ISCI process removes the restriction that the final state of the ion could only have  $^2P$  symmetry, which would be the result if only *final-ionic-state* configuration interaction (FISCI) is considered with a  $3p$  hole. In addition, one must not forget the case where the continuum electron in a primary  $3p \rightarrow \epsilon s, \epsilon d$  photoionization process inelastically scatters on its way out and excites an additional  $3p \rightarrow 3d$  transition. This final-state configuration interaction is an example of FISCI and leads to the same  $3s^2 3p^4 3d$  non- $^2P$  restricted final ionic states as the ISCI mechanism. The

inelastic scattering mechanism is particularly important in the threshold region.<sup>34,35</sup> Even under these conditions, the satellite excitation cross section will depend upon the  $3p \rightarrow \epsilon d$  excitation probability and should therefore in a gross manner follow the  $3p$ -ionization cross section in the low photon-energy region. This seems to be the observed behavior in the 40–60-eV photon-energy range.

Finally, because the relativistic effects are negligible in argon, the  $\beta$  factor for the  $3s^2 S$  main line and for the  $3s^2 3p^4 nd^2 S$  satellites 4, 5, and 6 is equal to 2 within the picture of FISCI, the  $3s$  derived  $3s^2 3p^4 nd^2 S$  satellites having the same  $\beta$  values as a function of kinetic energy. However, in reality the photoelectron wave function, and therefore the asymmetry parameter, will be different for each of the final ionic states. This can be described as an effect of FISCI. A Cooper minimum would therefore not occur precisely at the same kinetic energy for each channel. Krause *et al.*<sup>6(b)</sup> have investigated and confirmed such aspects with the  $5s$  photoelectron satellite spectrum of Xe which is suitable because there the  $5s$   $\beta$  factor shows strong deviations from the value of 2 in the region of the Cooper minimum. In this context it would also be very interesting to study the  $\beta$  variation of a clean monopole shakeup satellite such as  $2s^2 2p^4 3p^2 P$  in neon and its corresponding main line  $2s^2 2p^5 ^2P$ , from x-ray photoemission spectroscopy energies down into the threshold region, where screening effects due to the photoelectron will lower the satellite intensity and might influence the variation of the asymmetry parameter.

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- <sup>21</sup>We have recently observed the same autoionization of two-electron excitation neutral states not only in the  $3p$  partial cross section but also in the  $3s$  partial cross section. Using a C.I.S. technique<sup>9</sup> we have recorded a variation of the partial cross section which gives a precise value of the Cooper minimum position at  $42.3 \pm 0.2$  eV; the results will be published elsewhere.
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- <sup>26</sup>An error appeared in Table I of Ref. 7; it has been reported in the last column that satellites 3 and 4 derive 34% of intensity. In fact this 34% corresponds to the sum of the satellite's intensities in the adjacent column (58 eV). It was noticed elsewhere in the text that satellite 3 was not observed near the Cooper minimum because of the huge background signal for the lower electron kinetic energies.
- <sup>27</sup>The satellites arising from a "shakeup" process (FISCI)  $3s 3p 4p P$  are expected to have the same behavior as the main line; however, even in this case, when a  $3p$  hole is created, the two outgoing waves ( $1 \pm 1$ ) interfere with one another but may be different depending upon whether a second electron is excited or not. This leads to slightly different wave functions, consequently providing somewhat different  $\beta$  values for the main line and for the FISCI satellite. Moreover, there is a difference in kinetic energies at any photon energy.
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