Argon K suprathreshold structure

K. G. Dyall
Chemistry Department, Monash University, Clayton North, Australia 3168

R. E. LaVilla
Quantum Metrology Group, Center for Basic Standards, National Bureau of Standards, Washington, D.C. 20234
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The argon K absorption suprastructure features are assigned using *ab initio* calculations and tabulated experimental final-state energies. The assignments are supported by estimates of relative intensities. It is suggested on the basis of the analysis that the origin of the $K\beta''$ satellite is due to initial states with triple-vacancy $\underline{1s3p}^2$ core configurations.

The first measurements[1] of the onset and relative cross section of the argon $K\beta$ satellites showed the close relationship of their occurrence with the suprathreshold K absorption features. The $K\beta^V$ and $K\beta''$ satellites were attributed primarily to double-vacancy transitions from initial $\underline{1s3p}$ and $\underline{1s3s}$ hole states, respectively (the underline indicates vacancies in the subshell). As a part of that study, the argon K absorption spectrum was obtained with high statistics, and the KM region above threshold was found to have a rich structure. A preliminary identification of the KM region features was made with the aid of Hartree-Fock (HF) calculations[2] and use of the K I spectrum in the $Z+1$ approximation. Dyall and Grant[3] have recently calculated the argon $K\beta$ diagram and satellite spectrum taking into account correlation, relativistic effects, and relaxation, using extended shake theory to estimate the populations of the various double-vacancy configurations.[4] Also they have considered some triple-vacancy configurations. In light of the greater reliability of these estimates and some supplementary calculations, we present here a proposed reinterpretation of the argon K absorption structure above threshold.

Figure 1 shows the K absorption spectrum of Ar with the zero of the energy scale set to the $1s$ ionization threshold. Above the spectrum the calculated positions of various neutral, single-, double-, and triple-ion configurations are given. The energy regions of the single-ion states were taken directly from the calculations of Dyall and Grant.[3] The double-ion thresholds were arrived at by adding the calculated energy shifts from the diagram line of the double-ion x-ray transitions to the experimental energy differences between single- and double-ion final states from Moore.[5] Energies of excited double-ion configurations were determined by adding the calculated excitation energy to this threshold. A similar procedure was followed for triple-ion thresholds. Positions of neutral atom configurations were obtained from the difference between HF calculations on the particular configuration and the $\underline{1s}$ primary hole state. These were found to agree well with the positions predicted in the $Z+1$ approximation from the K I optical data. Although this approach does not include the correlations between bound electrons in the neutral atoms or the interaction of the various levels with the underlying continua—both of which would have to be taken into account for a rigorous identification of the features in the absorption spectrum—we believe there is sufficient accuracy in the calculated values for the positions of the configurations to provide tentative identifications for most of the absorption features which give rise to the satellites in the emission spectrum.

The notation of the spectral features in Fig. 1 is similar to that in Ref. 1. The features A and B are assigned to discrete transitions to the neutral configurations $\underline{1s3p}4s^2$ and $\underline{1s3p}4p^2$, respectively, as in Ref. 1. Between features A and B on the high-energy side of the valley, there is a slight enhanced absorption which is assigned to the neutral $\underline{1s3p}4s3d$ configuration. This transition is the conjugate of the transition to the $\underline{1s3p}4s^2$ configuration. Feature C is in good correspondence with the predicted position of the $\underline{1s3p}4p5p$ configuration. Higher members of the $\underline{1s3p}4pnp$ series would be weak and difficult to resolve. The limit of this series is expected to fall between features C and D. Feature D has an asymmetric shape reminiscent of a Fano profile. The shape and position of D are consistent with assignment to the $\underline{1s3p}5p^2$ configuration interacting with the $\underline{1s3p}4p\epsilon p$ continuum to produce the asymmetric shape. Above D the higher series $\underline{1s3p}npn'p$, n, $n'>5$ will occur at a fairly close spacing, and would be difficult to individually resolve. The broad feature E may be associated with the $\underline{1s3s}4s4p$ configuration. It corresponds to an increase in the gradient of the energy dependence of the β^V satellite intensity, consistent with the opening of a new decay channel. Coinciding with it are the thresholds for the $\underline{1s3p}$ double ion. The large width of this feature can be qualitatively explained by the onset of these continua and the Coster-Kronig decay of the $\underline{1s3s}4s4p$ configuration to $\underline{1s3p}4l$ configurations. We will return to feature E later.

Estimates of relative intensities of these features have been made using two approaches: one was a simple shake-up model, with values of the relevant overlap and dipole integrals from single-configuration Dirac-Fock cal-

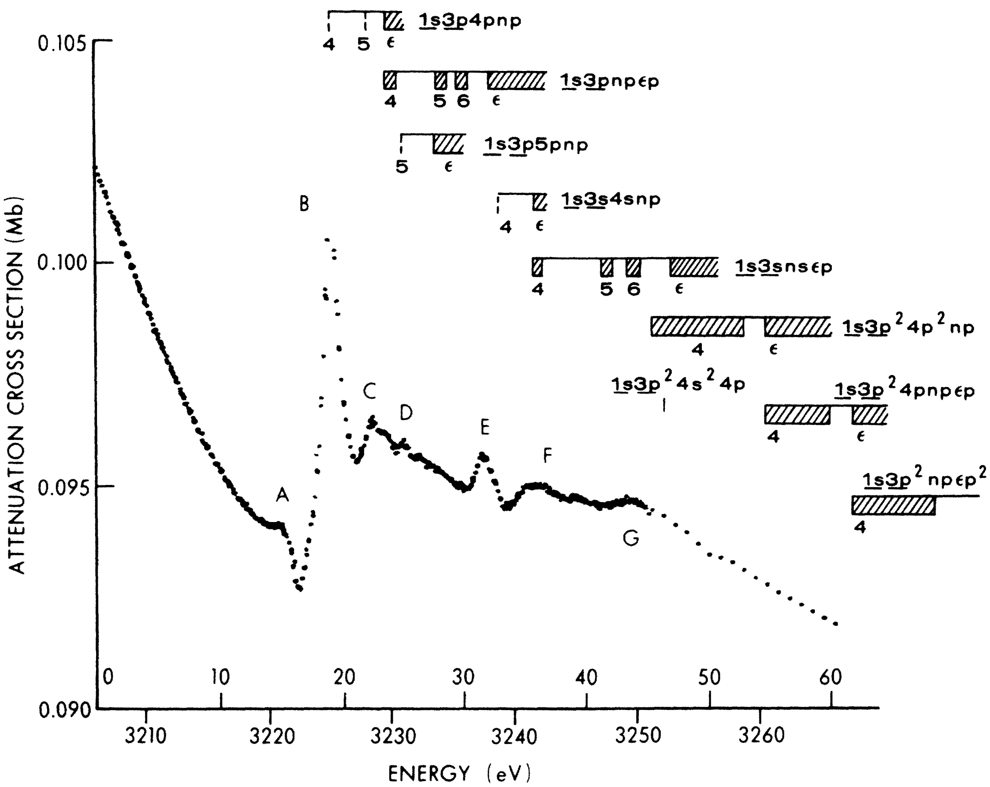

FIG. 1. Argon K absorption suprathreshold structure from Ref. 1.

culations, the other was a frozen-orbitals configuration-interaction (CI) model based on $1s$ hole-state wave functions, including the neutral atom, $3pnp$, $3p^2npn'p$, $1snp$, and $1s3pnpn'p$ configurations with n, $n'=4,5$. The results are given in Table I. The shake-up model results are in reasonable agreement with the CI model, except for the $1s3p4p5p$ configuration. The agreement of predicted intensities of the spectral features with experiment supports the assignments made above.

Above feature E there is less sharp structure. Feature F can plausibly be associated with the onset of the $1s3s4s\epsilon p$ continuum and the Rydberg states leading up to it. Above F one expects the series of states $1s3snsn'p$ converging on the $1s3sns$ limits, all of which will be broadened by Coster-Kronig decay. These continue through the (featureless) region G up to the $1s3s$ double ionization thresholds at 47 and 48 eV. The first triply excited neutral, $1s3p^2 3d4s4p$ should appear at about 40 eV. The spread of multiplets within this configuration, combined with their relatively small excitation intensities and the occurrence of states based on the $1s3s$ configurations should contribute so many small features to the spectrum that it would be very difficult to observe them separately, hence the relative featurelessness of the absorption in this region. The states based on the $1s3p^2$ configuration with two or three Rydberg electrons will probably autoionize to states based on the $1s3p$ configuration but more slowly than those based on the $1s3s$ configuration, since the decay is an Auger rather than a Coster-Kronig process.

At 50 eV there is a dip in the absorption spectrum followed by a slight rise at 52 eV. These features are in close proximity to the $1s3p^2 4p^3$ and $1s3p^2 4s^2 4p$ neutral atoms whose average energies differ by only 1 eV (see Table II). The multiplet spread of the $1s3p^2 4p^3$ configuration[6] is about 7.5 eV, straddling the 50-eV dip. It is very possible

TABLE I. Relative intensities of absorption features from shake-up and configuration-interaction calculations.

Configuration	Spectral feature	Relative intensity (%) Shake-up model	CI model
$1s4p$		100	100
$1s5p$		33	27
$1s3p4p^2$	B	8.5	12
$1s3p4p5p$	C	5.1	1.5
$1s3p5p^2$	D	0.5	0.2
$1s3s4s4p$	E	1.4	
$1s3p^2 4p^3$	G	0.3	

TABLE II. Energy of KM configurations of argon from nonrelativistic Hartree-Fock calculations.

Argon configuration	Center of gravity energy (a.u.)	Energy above $1s$ (eV)
$1s3p5p^2$	408.478 243	24.75
$1s3s4p5s$	407.910 891	40.19
$1s3p^2 4s^2 4p$	407.868 092	46.36
$1s3p^2 4p^3$	407.647 567	47.35
$1s3s3p4s4p^2$	407.043 845	53.78
$1s$	409.387 870	0

that the $\underline{1s3p^2}4s^24p$ configuration has a comparable multiplet spread. These features are tentatively assigned to triple-vacancy neutral atoms which could be considered a double shake-up transition accompanying the $4p\leftarrow 1s$ dipole transition. It is in this region of excitation that the β'' satellite starts to appear with measurable intensity.[1] The initial-state candidates for the origin of the β'' satellites are $\underline{1s3s}nln',\epsilon l$ and $\underline{1s3p^2}4p^2n,\epsilon l$ core states. We assigned feature E to the $\underline{1s3s}4s4p$ configuration and mentioned its correspondence to the increase of β^V emission intensity. This was attributed to the increase of $\underline{1s3p}nl$ initial states from the Coster-Kronig decay of $\underline{1s3s}4s4p$ core states. However, not all the $\underline{1s3s}4s4p$ states produced decay by Coster-Kronig process since the width of feature E is only about one-and-a-half times that of the prominent $\underline{1s3p}4p^2$ feature (B). In fact, if the Coster-Kronig rate was rapid enough to convert all the $\underline{1s3s}4s4p$ states to $\underline{1s3p}nl$ states, the resulting large breadth of feature E would probably render it indistinguishable from the background. If β'' were due to $\underline{3s3p}\leftarrow\underline{1s3s}$ transitions, some emission intensity should be evident before 50 eV. Thus, the radiative decay of $\underline{1s3s}$ core states contributes to the β^V complex.

The coincidence of the appearance of β'' emission with the thresholds for triple-core vacancy states suggests that this might be the correct origin of β'' initial states; theory[3] predicts that β'' originates from $\underline{3p^3}\leftarrow\underline{1s3p^2}$ transitions with or without Rydberg spectators. Although $\underline{1s3s}$ thresholds occur in the region of feature G, the argument above negates their contribution to β'' emission intensity. Recent work[7] has shown that the shake-off intensities predicted by Dyall[4] are much lower than the experimental values; thus the predicted β'' intensity[3] will also be too low. This further substantiates the assignment of β'' to $\underline{3p^3}\leftarrow\underline{1s3p^2}$ core transitions. There is an increase in the intensity of β'' between 63 and 78 eV (which is the triple-ion threshold). A plausible explanation for this is that above 63 eV it is not possible to form neutral or singly-ionized states which can decay to states based on the $\underline{1s3p}$ configuration. Therefore, the $\underline{1s3p^2}nl$ core states can only contribute to β'' and not to β^V emission to final $\underline{3p^2}nl$ states. This would give further support for the assignment of β'' to transitions from states with a $\underline{1s3p^2}$ core vacancy configuration.

CONCLUSIONS

From the simple approach adopted here, it appears possible to make reasonable assignments for all the features of the argon K absorption suprathreshold structure that are consistent with the threshold measurements of the argon $K\beta$ satellite spectrum. Further experimental work is needed to clarify some points, e.g., the onset of β''. Complementary experiments such as the measurement of secondary-electron spectra as a function of photon energy could also be useful in verifying the explanations given for the absorption features. Additional theoretical work is needed to provide a more complete and rigorous explanation of both the absorption and emission spectra.

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