Threshold Double Photoexcitation of Argon with Synchrotron Radiation

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Auger satellites have been measured to determine the probability of M-shell excitation accompanying K-shell photoionization of Ar, as a function of photon energy. The theoretically predicted difference between the dependence of shakeup and shakeoff probabilities on the photon energy near threshold is demonstrated for the first time. Results are critically compared with calculations.

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In atomic inner-shell photoionization, multiple excitation processes occur with significant probability. The resulting final states are approximately described by configurations formed by removal of a core electron and excitation of additional electrons to higher bound states (shakeup) or to the continuum (shakeoff).[1-3] Such multiple excitation processes result in satellites in the photoelectron spectra[1,4-6] and in the Auger and x-ray spectra from transitions through which the photoexcited states decay.[2,7,8] The study of these multiple excitation processes is important because they epitomize the breakdown of the independent-particle model and can provide important clues for the understanding of electron correlation and of excitation dynamics.[3,5,9,10] The energy dependence of the cross sections for double excitation is particularly informative near threshold; the observation of Auger satellites makes it possible to measure this dependence. Here we report on an investigation in which highly monochromatized, hard synchrotron radiation was tuned through the thresholds for various multiple-excitation processes during $1s$ ionization of Ar, and the probabilities of accompanying $3s$ and $3p$ excitation were traced by measurement of the intensities of pertinent Auger satellites. Results are compared with theory.[3,10]

In the experiment, x rays from an eight-pole wiggler, operating at 14 kG, were focused onto an Ar jet by a Pt-coated doubly curved toroidal mirror. The x-ray bandwidth from a Ge(111) double-crystal Bragg monochromator was 0.9 eV at $h\nu = 3200$ eV; the flux on target was $\sim 10^{12}$ photons/s with 60 mA of 3-GeV electrons in the SPEAR storage ring. Electron spectra were measured with a computerized double cylindrical-mirror analyzer; with a pass energy of 82.5 eV, the electron-spectrometer resolution was 1.6 eV.

We take the 2660-eV Ar K-L_2L_3 $^1D_2$ Auger-electron line as reference. The K-LL Auger yield[11] of Ar is affected only minutely by excitation of one or two M-shell electrons. The intensity of satellites of the ^1D Auger line relative to that of the "diagram" line is therefore a measure of the probability of the multiple photoexcitation processes studied here.

To interpret the ^1D Auger satellite spectrum it is necessary to calculate the radiationless transition energies and rates in the presence of one or two open M subshells. The initial states can be limited to those which in the sudden approximation are expected to be significantly populated.[1] These are the $[1s3l]$ ($l = 0, 1$) shakeoff states and the $[1s3l]nl$ ($n = 4$ and 5 for $l = 1$, $n = 4$ for $l = 0$) shakeup states, where square brackets indicate hole states. In the limited $3s\,(^2S)ns\ ^{1,3}S\,1s\ ^2S$ and $3p^5(^2P)np\ ^{1,3}S\,1s\ ^2S$ basis, the eigenstates are linear superpositions of ^1S and ^3S states. The initial shakeup states can be identified as states with dominant ^1S component because the monopole selection rules prevent transitions to the triplet state. According to our Hartree-Fock (HF) calculations, the initial $[1s3p]4p$ state has almost pure ^1S character, whereas in the other shakeup cases the mixture is more uniform.

The radiationless decay of the initial doubly excited states considered above to the various $[2p^2(^1S,\,^1D)3l]nl\ ^{1,3}L$ final states was analyzed by calculation of transition energies as differences between initial-and final-state total energies. The states were described by single-configuration HF configuration-average wave functions in *LS* coupling. Relative transition rates within each multiplet were calculated from the square of the product of appropriate angular factors and Slater integrals. The ratio of the *s*- to *d*-wave contributions to the K-$L_{2,3}L_{2,3}\,{}^1S$ and ${}^1D$ transition rates was estimated with Hartree-Slater wave functions. Nonresonant triple-excitation satellites fall outside the energy span of the spectra.

Calculated Auger satellite energies are indicated schematically in Fig. 1. The satellites arising from 3*s* and 3*p* shakeoff accompanying 1*s* ionization are seen to fall into the peak around ~ 2643 eV, while most 3*s* and 3*p* shakeup processes cause Auger satellites that fall within the 2650-eV peak, unresolved from the K-$L_2L_2\,{}^1S_0$ diagram line. The measured intensity of the ${}^1S$ line, excited below the threshold for any [1*snl*] double processes, is $(11.0 \pm 0.6)\%$ of the ${}^1D$-line intensity, in excellent agreement with the prediction (11.12%) from a relativistic intermediate-coupling calculation that includes configuration interaction.[11] The predicted positions of the Auger lines are only slightly affected by configuration mixing in the initial states and by relativity.

In Fig. 2(a), the relative intensity of the 2650-eV shakeup satellite peak including the ${}^1S_0$ diagram line is plotted. The satellite peak that arises at photon energy $E = 3225$ eV is tentatively ascribed to the $[1s3p]4p^2$ bound-bound resonance, in accordance with the interpretation of the Ar *K*-absorption spectrum[8] which shows a peak at 3224 eV. In accord with observations of Kobrin *et al.*,[6] the [1*s*3*p*]4*p* shakeup satellite appears to have approximately half its asymptotic intensity at 5 eV above threshold. Saturation of [1*s*3*p*]4*p* plus opening of the [1*s*3*s*]4*s* channel lead to a small gradual increase which levels off to a constant shakeup satellite intensity ~ 60 eV above the [1*s*3*p*]4*p* threshold.

Within the independent-electron model, the shakeup cross section is given by a combination of monopole and dipole *radial* matrix elements, $\langle n'l|nl\rangle$ and $\langle n'l'|r|nl\rangle$, respectively. If we neglect terms with double- and triple-order products of the $n' \neq n$ overlap elements, the ratio of the [1*s*3*p*]4*p* to [1*s*] cross sec-

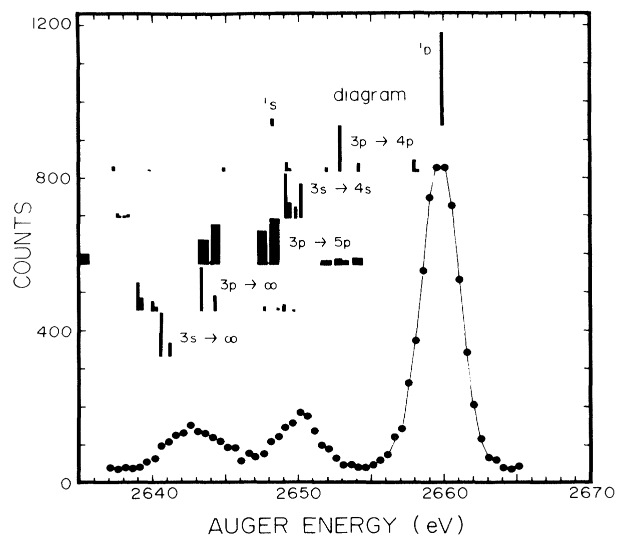

FIG. 1. Calculated energies of Auger satellites caused by 3*s* and 3*p* electron excitation accompanying 1*s* ionization, with reference to an Ar K-$L_{2,3}L_{2,3}$ Auger spectrum photoexcited 2000 eV above the 1*s* ionization threshold. Estimates of relative satellite intensities within each multiplet are indicated by the heights of the bars.

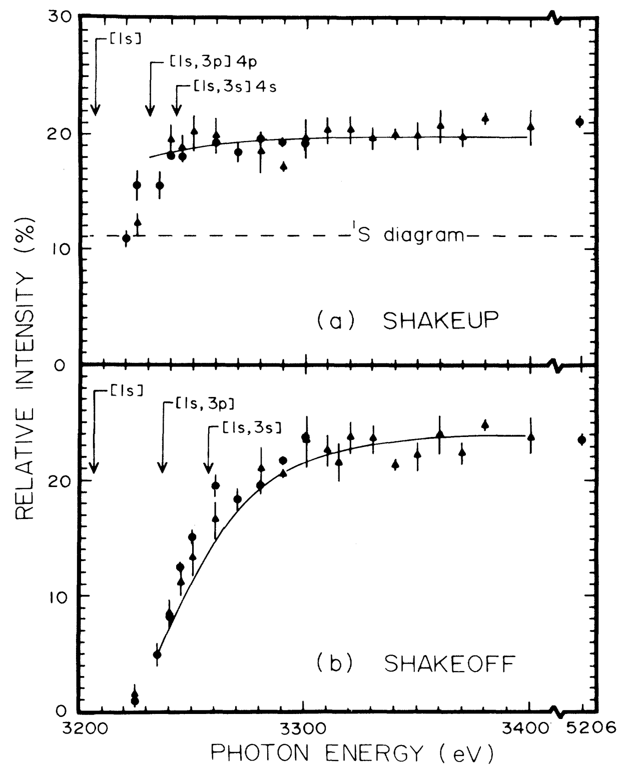

FIG. 2. (a) Intensity of the 2650-eV feature in the photoexcited Ar K-$L_{2,3}L_{2,3}$ Auger spectrum, with reference to the ${}^1D$ line intensity, as a function of x-ray energy. The dashed line at 11.1% indicates the ${}^1S$ diagram-line contribution. Energy thresholds for 1*s* ionization and for $3p \rightarrow 4p$ and $3s \rightarrow 4s$ shakeup accompanying 1*s* ionization are indicated by vertical arrows. The normalized theoretical prediction for the near-threshold energy dependence of these relative shakeup probabilities is represented by the solid curve. (b) Photoexcitation-energy dependence of the 2643-eV Auger satellite-group intensity. Thresholds for 1*s* ionization alone and accompanied by 3*p* and 3*s* ionization are indicated by vertical arrows. The normalized theoretical relative shakeoff probability is indicated by the solid curve. Circles and triangles pertain to data from separate experiments.

tions is[3]

$$R_{3p\to 4p}(E)=P\{[1s\,3p]4p\}\{5A_+(\epsilon_1)^2+7A_-(\epsilon_1)^2\}/2P\{[1s]\}\langle\epsilon' p|r|1s\rangle^2, \tag{1}$$

where

$$A_\pm(\epsilon_1)=\langle 4p|3p\rangle\langle\epsilon_1 p|r|1s\rangle\pm\langle\epsilon_1 p|3p\rangle\langle 4p|r|1s\rangle$$

and

$$P\{[n_1l_1\ldots]n_2l_2\}=\prod_{n,l}\langle nl|nl\rangle^{2q(nl)}.$$

Here, $q(nl)$ is the number of electrons in subshell nl of the hole configuration $[n_1l_1\ldots]$. From energy conservation, we have $\epsilon_1=E-I\{[1s\,3p]4p\}$ and $\epsilon'=E-I\{[1s]\}$, which leads to the E dependence indicated by the solid curve in Fig. 2(a). The continuum wave function was calculated in a $[1s\,3p]4p$ HF frozen core, with use of Seaton's method.[12] The theoretical curve was normalized to the measured point at $E=3370$ eV, whereas the calculated asymptotic intensity ratio $R_{3p\to 4p}(\infty)$ [Eq. (1)] is 14%. The measured energy dependence of the shakeup probability is seen to be well predicted by theory, except very close to threshold. The configuration-interaction calculation of Dyall[10] includes mixing between $[1s\,3l]4l$ and higher members of that shakeup series. The *shape* of the curve is not much affected by this configuration interaction, but a shifting of intensities results, from the lower to upper states.

In contrast to shakeup, double-ionization cross sections *must* always start from zero at the threshold,[3] as can be seen from the independent-electron-model cross-section ratio

$$R_{3p\to\epsilon p}(E)=P\{[1s\,3p]\}\int_0^{\epsilon_2}\{5A_+(\epsilon)^2+7A_-(\epsilon)^2\}d\epsilon/4P\{[1s]\}\langle\epsilon' p|r|1s\rangle^2, \tag{2}$$

where we have $\epsilon_2=E-I\{[1s\,3p]\}$. The $4p$ wave function in Eq. (1) is replaced by the continuum wave function of the shakeoff electron with energy ϵ $(0\leqslant\epsilon\leqslant\epsilon_2)$, so that $\epsilon_1=\epsilon_2-\epsilon$. It is clear from Fig. 2(b) that the measured cross section does *not* go to zero at the $[1s\,3p]$ threshold. This fact can be attributed to admixture, in the 2643-eV peak, of satellites due to half of the $3p\to 5p$ excitations and higher shakeup, according to our energy calculations.

If we assume in accordance with Fig. 2(a) that the shakeup ratio is practically constant as a function of E, then it can be concluded that the experimental shakeoff curve levels off at high E at $(19\pm 2)\%$ (after subtracting the threshold value of 5%). The *shape* of the curve is well predicted by a calculation of the ratio given by Eq. (2), using HF wave functions for both the $[1s\,3p]$ core and continuum states [Fig. 2(b)]. In the calculation of the continuum wave functions the Lagrangian multipliers were neglected, but a Schmidt orthogonalization was carried out afterwards. As seen in Fig. 2(b), the measured cross-section curve is only slightly affected by the opening of the $[1s\,3s]$ shakeoff channel. Our calculations predict an asymptotic shakeoff probability of 25% at high E.

Dyall[10] has estimated the $[1s\,3s]$ and $[1s\,3p]$ relative shakeoff probability by in essence taking the total shake probabilities $1-\langle nl|nl\rangle^2$ per electron and subtracting the shakeup probabilities calculated from Rydberg nl $(n\geqslant 4)$ functions generated in a frozen-core average-of-configuration potential for the $[1s\,3s]$ and $[1s\,3p]$ configurations. The result, 7.3%, is only one-third of our experimental probability, $(19\pm 2)\%$. In order to understand this discrepancy, it is useful to examine the sudden $3p$ shakeup-shakeoff limit[3]

$$R_{3p\to n(\epsilon)p}(\infty)=\frac{6(1-\langle 3p^*|3p\rangle^2)}{\langle 3p^*|3p\rangle^2},$$

in which the small influence of the forbidden transition $\langle 2p^*|3p\rangle^2$ has been neglected. (We now denote the hole-state $3p$ wave function by an asterisk.) If the $|3p^*\rangle$ wave function is chosen as the one which corresponds to the $[1s\,3p]$ core, the result is 37%. If this wave function is chosen, on the other hand, as that which corresponds to the $[1s]$ core, as in the conventional sudden-approximation method, then the result is 20.5%. Subtraction of the $\sim 12\%$ $[1s\,3p]nl$ shakeup intensity[10] from the first of these results leads to 25% shakeoff; subtraction from the second result gives 9% shakeoff. It appears that the $3l^*$ wave functions of Ref. 10 were generated in a one-hole potential, different from the potential that was used in generating the Rydberg orbitals.

The total shakeup-shakeoff probability at large E that we measure is $(33\pm 4)\%$. This is somewhat higher than the total M shake probability of $(26\pm 2)\%$ measured by Krause, Carlson, and Dismukes[1] and also slightly exceeds the relative K x-ray satellite intensity of $(28\pm 2)\%$.[2,8] The corresponding conventional shake value calculated from Dirac-Fock (DF) wave functions, including forbidden-transition corrections, is 24.4%.

We can draw the following conclusions: (1) The difference in the photon-energy dependence of shakeup versus shakeoff close to threshold has been shown experimentally, for the first time, to be as predicted by theory. (2) The measurements indicate more shakeoff than shakeup at high photon energy, in contrast to the predictions of Ref. 10 but in accord with Ref. 1. (3) The measured shakeup probabilities agree well with the predictions of Ref. 10, but the shakeoff probabilities do not. (4) The measured total shake probabilities are bracketed by the sudden-approximation values calculated by the HF (DF) method for a double-hole $[1s3l]$ and a single-hole $[1s]$ field. Within the restricted HF (DF) method, both procedures are somewhat inconsistent with respect to fulfilling the closure relation. This inconsistency could be removed if many-electron wave functions were used to obtain the

$$\langle \bar{\phi}([1s3l]n(\epsilon)l)^2S \,|\, \phi_{\text{frozen}}([1s])^2S \rangle$$

shakeup and shakeoff amplitudes, since the $\bar{\phi}$ functions are eigenfunctions of the *same* projected $(N-1)$-electron Hamiltonian $PH(N-1)P$, where $P = |1s\rangle\langle 1s|$.

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[1]M. O. Krause, T. A. Carlson, and R. D. Dismukes, Phys. Rev. **170**, 37 (1968).

[2]T. Åberg, Phys. Rev. **156**, 35 (1967).

[3]T. Åberg, in *Proceedings of the International Conference on Inner-Shell Ionization Phenomena and Future Applications,* edited by R. W. Fink, S. T. Manson, J. M. Palms, and P. Venugopala Rao, U.S. AEC Report No. CONF-720404 (National Technical Information Service, U.S. Dept. of Commerce, Springfield, Va., 1972), p. 1509.

[4]U. Gelius, J. Electron Spectrosc. **5**, 985 (1974).

[5]R. L. Martin and D. A. Shirley, in *Electron Spectroscopy,* edited by C. R. Brundle and A. D. Baker (Academic, New York, 1977), Vol. I, Chap. 2.

[6]P. H. Kobrin, S. Southworth, C. M. Truesdale, D. W. Lindle, U. Becker, and D. A. Shirley, Phys. Rev. A **29**, 194 (1984).

[7]L. Asplund, P. Kelfve, B. Blomster, H. Siegbahn, and K. Siegbahn, Phys. Scr. **16**, 268 (1977).

[8]R. D. Deslattes, R. E. LaVilla, P. L. Cowan, and A. Henins, Phys. Rev. A **27**, 923 (1983).

[9]M. Ya. Amusia, Adv. At. Mol. Phys. **17**, 1 (1981).

[10]K. G. Dyall, J. Phys. B **16**, 3137 (1983).

[11]M. H. Chen, B. Crasemann, and H. Mark, Phys. Rev. A **21**, 436, 442 (1980).

[12]M. H. Chen, B. Crasemann, M. Aoyagi, and H. Mark, Phys. Rev. A **18**, 802 (1978).