Synchrotron Radiation Studies of the Ar $3s^{-1}$ Binding-Energy Spectrum: A Comparison of Experimental Intensities and Theory

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The argon $3s^{-1}$ photoelectron spectrum has been measured with tunable synchrotron radiation (80–130 eV). The intensity of the $3s^23p^43d(^2S)$ satellite at 38.6 eV, relative to the main $3s3p^6(^2S)$ line at 29.3 eV, *increases* with increase in photon energy contrary to recent theoretical predictions. The intensity ratio increases towards the value given by electron momentum [binary $(e, 2e)$] spectroscopy.

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Currently, a serious disagreement exists[1-7] between experiment and theory as to the relative intensities of main and satellite lines in noble-gas ns^{-1} inner-valence binding-energy spectra. Inconsistencies also exist between measurements obtained by photoelectron spectroscopy[8] and by electron-momentum spectroscopy.[9-13] The present work resolves this disagreement by new experimental measurements using photoelectron spectroscopy and monochromatized synchrotron radiation. Results indicate that existing theory[2-7] is inadequate.

A quantitative description of satellite structures in binding-energy spectra is needed for a more complete understanding of correlation (many-body) effects in the ionization of atoms and molecules. Such effects are notably manifested by the ns^{-1} inner-valence ionization of the noble-gases Ar, Kr, and Xe ($n = 3$, 4, and 5, respectively), and the corresponding binding-energy spectra have been the subject of a number of theoretical and experimental studies.[1-13] In particular, the argon $3s^{-1}$ spectrum is a test case which has received particular experimental attention[8-11] because argon is readily available, while from a theoretical standpoint its treatment,[1-7] unlike that for the heavier noble gases, has not been considered to require incorporation of relativistic effects.

Energies and intensities in the Ar $3s^{-1}$ binding-energy spectrum have been studied by photoelectron spectroscopy (PES) at low photon energies (UPS) by Adam and co-workers[14,15] using tunable synchrotron radiation and magic-angle PES over the photon energy range 40–77 eV. The most recent work[15] has also reported measurements of asymmetry parameters β for various satellites in the $3s^{-1}$ spectrum. Early studies of the Ar $3s^{-1}$ spectrum were made by Spears, Fishbeck, and Carlson (SFC) using x-ray photoelectron spectroscopy (XPS) with x-ray lines at photon energies of 151, 1254, and 1487 eV.[8] These line sources were used without any dispersion of the radiation and measurements were made at an ejection angle of 90° rather than the magic angle. Therefore, the relative satellite intensities[8] are not necessarily expected to reflect accurately the true relative partial cross sections because of different β dependences, as has recently been discussed for xenon by Fahlman *et al.*[16] In addition to these uncertainties, backgrounds in the SFC data[8] are quite large and not necessarily flat, causing the correctness of the relative intensities estimated from this data to be in question. The nature of the background[8] and its effects on relative satellite intensities have recently been discussed in a paper by Mitroy, McCarthy, and Weigold.[1]

An alternative method of measuring binding-energy spectra is electron-momentum spectroscopy (EMS) —also formerly known as *binary* $(e, 2e)$ spectroscopy.[9] This technique has been used to study the Ar $3s^{-1}$ spectrum on numerous occasions and recently two independent EMS studies,[10,11] at improved energy resolution, have permitted more accurate assessment of the individual satellite and main-line relative intensities than does earlier work.[9] Furthermore, the high impact energies employed [1200 eV (Ref. 10) and 1000 eV (Ref. 11)] ensure the effective validity of the plane-wave impulse approximation used to extract quantitative data.[13] Under these conditions EMS is expected to give the satellite relative intensities directly,[9,17] free of any factor such as the photon-energy–dependent dipole matrix term which is included in PES spectral intensities. Therefore EMS satellite relative intensities are expected to be suitable for direct comparison with theoretically calculated transition probabilities (pole strengths) for satellites in the same symmetry manifold, as has been discussed by McCarthy.[17] Furthermore, it is expected that relative satellite and main-line intensities, within a given symmetry manifold, should be comparable in EMS and *high-energy* PES (i.e., XPS) since in the latter the dipole matrix element should be essentially constant over the spectral range. These considerations and a comparison of theory with EMS and PES spectra at high and low photon energy have been discussed earlier for the OCS molecule.[18,19] However, the relative intensities in the EMS spectra[10,11] for the Ar $3s^{-1}$ spectrum are in significant disagreement with the XPS results reported by Spears, Fishbeck, and Carlson.[8]

Configuration-interaction calculations of the Ar $3s^{-1}$ spectrum reported by Dyall and Larkins (DL)[7] and also by Smid and Hansen[2-6] are in reasonable agreement with each other, particularly with regard to the relative intensities of the main 3s line $[3s3p^6(^2S)]$ at 29.3 eV and the most intense satellite [dominant configuration $3s^23p^43d(^2S)$] at 38.6 eV. Furthermore, these calculations[2-7] are also in reasonable agreement with the XPS results tabulated by Spears, Fishbeck, and Carlson[8] despite the β-dependency and baseline uncertainties in these experiments (see above comments).

On the basis of the above findings, and also considering the low-photon-energy data of Adam and coworkers,[14,15] Smid and Hansen have suggested[3-6] that there may therefore be difficulties in the interpretation (reaction model) of EMS [binary $(e,2e)$] spectroscopy. Furthermore, on the basis of their calculations and the XPS[8] and low-energy PES[14,15] measurements, Smid and Hansen[5] have predicted that the intensity of the main satellite line relative to the main line [i.e., $3s^23p^43d(^2S)/3s3p^6(^2S)$] in the Ar $3s^{-1}$ spectrum should *increase* with *decrease* in photon energy. The situation is also further complicated by the configuration-interaction calculation for the Ar $3s^{-1}$ spectrum by Mitroy, Amos, and Morrison[20] which gives results much closer (see Table 8 of Ref. 20) to the relative intensities as observed in EMS but which are in disagreement with the XPS results.[8] This controversy has been further heightened by the recent article by Mitroy, McCarthy, and Weigold,[1] questioning the correctness of both the Hansen theory[2-5] and the XPS measurements.[8] A further paper by Smid and Hansen[6] questions the theoretical work of Mitroy, Amos, and Morrison.[20]

In order to resolve this complex situation and the apparent disagreements between theories and between theory and experiment, as well as to resolve the question of the validity of the interpretation of EMS experiments, we now report new synchrotron-radiation PES measurements for the Ar $3s^{-1}$ spectrum in the photon energy range 80–130 eV. The present measurements were made with a Leybold LHS-11 magic-angle photoelectron spectrometer[21] together with a Mark IV Grasshopper monochromator.[22] The photon energy range above 80 eV avoids the prominent Ar 3s Cooper-minimum effects found at lower photon energies and demonstrated in the elegant experiments reported by Adam, Morin, and Wendin.[15] The upper limit of 130 eV photon energy, dictated by the 200-MeV Tantalus storage ring, is nevertheless sufficiently close to the lowest XPS energy (151 eV) used by SFC[8] to provide a reasonable consistency check on the earlier work. At $h\nu = 130$ eV the dipole matrix element can be considered essentially constant[5] over the range of binding energies involved. At the lowest photon energies used in the present work (80 eV) quantitative comparison with the work of Adam *et al.*[14] at 77 eV provides a further consistency check as illustrated by the almost identical spectra shown in Fig. 1. The relative intensity of the $3s^23p^43d(^2S)$ satellite at 38.6 eV is the main focus of the present study.

A series of PES spectra for Ar $3s^{-1}$ have been recorded in the photon energy range 80–130 eV at an energy resolution of 1.7 ± 0.1 eV FWHM in order to facilitate direct comparison of intensities with the recently reported EMS spectra.[10,11] This resolution is also comparable with that used in the XPS work of Spears, Fishbeck, and Carlson.[8] The EMS spectra[10,11] and the earlier low-energy PES spectra[14,15] indicate

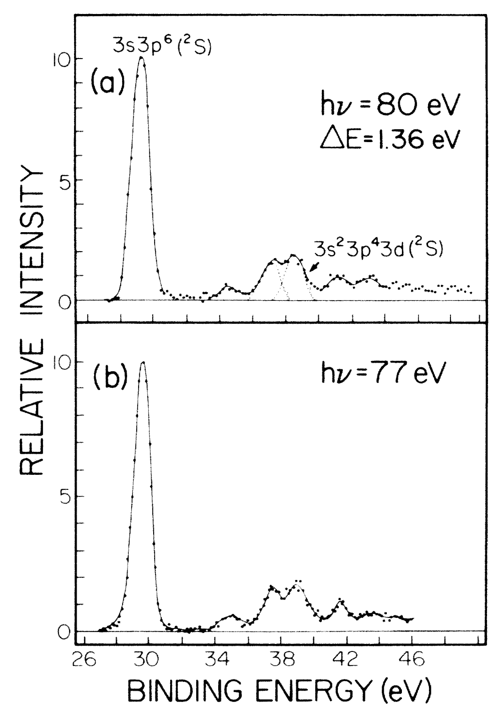

FIG. 1. Argon $3s^{-1}$ magic angle photoelectron spectra: (a) this work, and (b) Ref. 14.

that the intensities of the main line $[3s3p^6(^2S)]$ at 29.3 eV and the first major satellite $[3s^23p^43d(^2S)]$ at 38.6 eV should be effectively free at their peak maxima of overlapping contributions from neighboring states. Relative intensities can therefore be obtained from peak areas or more simply from peak heights since the resolution is sufficiently good and single states are involved. In practice, area comparison has also been considered as a cross check and the present results and conclusions are independent of the small variations in resolution shown for the two spectra in Fig. 2. In this regard it should be noted that the peak at ~ 37 eV, on the low-energy side of the $3s^23p^43d(^2S)$ line, decreases relative to the latter as the photon energy increases (it can also be seen that this peak at ~ 37 eV is of relatively low intensity in the EMS spectra[10,11]). This effect is illustrated in Fig. 2 which shows spectra at $h\nu = 80$ and 120 eV. Clearly the relative contribution of the $3s^23p^43d(^2S)$ peak at 38.6 eV has increased with photon energy compared to that of the main line. This trend is maintained throughout the photon range 80–130 eV and the intensity ratio $R = 3s^23p^43d(^2S)/3s3p^6(^2S)$ *increases* steadily with *increase* in photon energy from a value of 0.21 at 80 eV to 0.28 at 130 eV as shown in Fig. 3. This general conclusion of the increase of R with increase in photon energy is independent, within experimental error, of whether peak heights or areas[23] are used or of any uncertainty in the spectral base line. The datum point of Adam and co-workers[14,15] at 77 eV smoothly adjoins the present data which are apparently converging at the higher photon energies. We have placed the ratio (0.32 ± 0.02) as given by both of the latest EMS experiments[10,11] at the zero of the $1/E$ axis to assume the position of the high-photon-energy limit in keeping with the ideas discussed by McCarthy[17] and also by Cook *et al.*[18] The ratio (0.27) reported by Mitroy, Amos, and Morrison[20] is in better agreement with the EMS data and the projections from the present PES work than with the values of 0.135 and 0.13 calculated at 1487 eV by Hansen and Smid[3-5] and by Dyall and Larkins,[7] respectively. The present work is also inconsistent with the XPS results of Spears, Fishbeck, and Carlson.[8] Considering the trend of the present results at 130 eV and the background uncertainties and β dependence of the latter work[8] the XPS results must be considered questionable from an intensity standpoint. If this is the case then the theoretical calculations[2-7] would also be significantly incorrect. Certainly the fact that the relative satellite intensity is experimentally observed to increase with increase in photon energy [this is true not only for the $3s^23p^43d(^2S)$ but also for the *total* satellite to main line intensity[23]], which is exactly the opposite of the predictions (see dotted line on Fig. 3) by Smid and Hansen,[5] casts doubt as to the accuracy of the calculations. In addition the fact that the results of the present PES measurements tend, at high photon energy, towards the value given by EMS[10,11] provides further support for the arguments advanced by McCarthy[17] and also by Cook *et al.*[18] These results appear to suggest that the present interpretation[9,11,17] of satellite intensities in EMS is probably substantially correct, although it should be remembered that whereas EMS probes preferentially the low-electron-momemtum part (0–2 a.u.) of the wave function, XPS probes the high-momentum part (~ 10 a.u. at 1487 eV). In this regard, however, the present PES result at 130 eV corresponds to a momentum of 2.7 a.u. which is comparable with the value (~ 3.0 a.u.) for

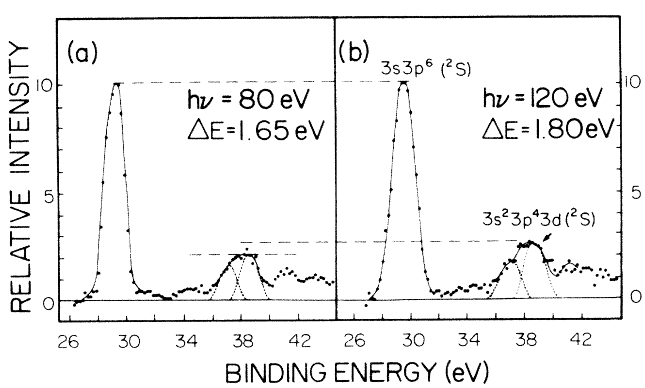

FIG. 2. Argon $3s^{-1}$ magic-angle photoelectron spectra.

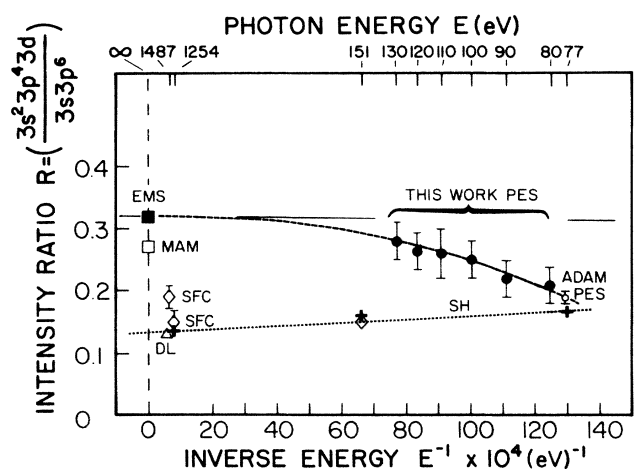

FIG. 3. Intensity ratio $R = 3s^23p^43d(^2S)/3s3p^6(^2S)$ as a function of inverse photon energy $10^4/E$. PES: solid circles, this work; open circles, Adam and co-workers (Refs. 14 and 15); open diamonds, Spears, Fishbeck, and Carlson (Ref. 8). EMS: the solid square represents the identical values obtained independently in Refs. 10 and 11. Theory: crosses, Smid and Hansen (Ref. 5); open triangles, Dyall and Larkins (Ref. 7); open square, Mitroy, Amos, and Morrison (Ref. 20).

the 151-eV XPS measurement.[8] In the case of Xe $5s^{-1}$ ionization by EMS, Weigold and co-workers[12,13] have found that satellite relative intensities are invariant within experimental error over the momentum range 0–2 a.u.

The present findings are supported by a more detailed PES study[23] of Ar $3s^{-1}$ ionization which is now being completed together with a corresponding study of Xe $5s^{-1}$ ionization in comparison with EMS measurements and theory. It is found[23] that the increase of satellite intensity relative to the main ns^{-1} line is even greater in the case of Xe than for Ar. In the meantime new high-energy XPS studies of the Ar $3s^{-1}$ ionization spectrum obtained at the magic angle are highly desirable to check directly the quantitative accuracy of the Spears, Fishbeck, and Carlson data[8] and to investigate the possibility that some different and unexpected photophysics is occurring above the limit of the present PES data at 130 eV.

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