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Satellite Intensities in Photoelectron Spectroscopy and Electron Momentum Spectroscopy—Synchrotron Radiation Studies of Argon 3s and Xenon 5s Photoionisation ($h\nu$ = 60–130 eV)*

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Abstract

Binding energy spectra for the main line, satellite lines and associated double ionisation continuum for argon 3s and xenon 5s photoionisation have been measured in the photon energy range 60–130 eV using monochromatised synchrotron radiation and magic angle photoelectron spectroscopy. In particular the ratio of satellite to main line intensities has been investigated and compared with the results of earlier experiments using X-ray and ultraviolet photoelectron spectroscopy as well as with recent measurements by electron momentum [i.e. binary (e, 2e)] spectroscopy. The results of the presently reported photoelectron measurements show that the satellite intensity relative to that of the main ns^{-1} line increases with increasing photon energy and approaches the value given by electron momentum spectroscopy. These findings are contrary to predictions based on recent calculations of photoelectron intensities. The present work lends support to the direct interpretation of satellite intensities (pole strengths or spectroscopic factors) in binary (e, 2e) spectroscopy using the plane wave impulse approximation. The need for improved calculations of photoionisation intensities as well as further photoelectron measurements in the X-ray region is stressed.

1. Introduction and Background

Satellite structure in binding energy spectra, particularly in the inner valence region, is of considerable interest since it arises from many-body (electron correlation) effects (i.e., a failure of the independent particle or orbital model) in the ionisation process. These effects can be described by using final ionic state configuration interaction (FISCI). Typical examples of such effects occur in the inner valence ns ionisation spectra of the noble gases argon, krypton and xenon for which there is a manifold of final ionic states of which the main line can be attributed to the dominant configuration $ns\,np^6(^2S)$ and the satellites to dominant configurations of the type $ns^2\,np^4\,nl$. The overall ns^{-1} parentage of the satellites has been convincingly demonstrated by measurements of initial state momentum distributions at the various binding energies using electron momentum [also known as binary (e, 2e)] spectroscopy (McCarthy and Weigold 1976; Leung and Brion 1983). The noble gas ns^{-1} main line and satellite spectra have been studied extensively by photoelectron spectroscopy (PES) both at low (ultraviolet) photon energies (UPS) below ~80 eV (Adam *et al.*

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1978*a*, 1978*b*, 1979, 1985; Fahlman *et al.* 1984*a*, 1984*b*; Suzer and Hush 1977) and also to a lesser degree by X-ray photoelectron spectroscopy (XPS) at generally much higher photon energies (1254 and 1487 eV) (Spears *et al.* 1974; Gelius 1974). At intermediate photon energies the only XPS study is the single measurement for Ar $3s^{-1}$ at 151 eV (Zr Mζ) by Spears *et al.* (1974).

For the development of theory correctly describing the many-body ionisation process, accurate measurements are needed not only of the main line and satellite binding (separation) energies but also, more importantly, of the correct relative intensities. Accurate intensity measurements require that PES measurements be made at the magic angle (54·7°) in order to eliminate the (often appreciable) effects of the final ionic state angular anisotropy parameter β (Adam *et al.* 1985; Fahlman *et al.* 1984*a*). A further requirement is that the electron analyser transmission efficiency (Brion and Hamnett 1981) be accurately known and applied to the measured intensities. The fact that most PES measurements for atoms and molecules usually have been made without adoption of either of these two criteria renders the data of little use for quantitative purposes such as comparison with calculated intensities. Since effects of β and transmission efficiency can often be appreciable, theorists and experimentalists should ensure that both factors have been taken into account when comparing PES measurements with calculations of intensities.

In the case of the noble gas ns^{-1} photoionisation studies listed above, the XPS work reported by Spears *et al.* (1974) for argon, krypton and xenon, by Gelius (1974) for xenon, as well as the UPS work for xenon at 40·08 eV (304 Å) by Suzer and Hush (1977), were all determined at a photoelectron ejection angle of 90° rather than at the magic angle. In addition none of these spectra were apparently corrected for transmission, although this omission may not be too serious, at least in the case of the XPS study, since the relative kinetic energy variation over the spectrum is small. The remaining PES studies of the noble gases (Adam *et al.* 1978*a*, 1978*b*, 1979, 1985; Fahlman *et al.* 1984*a*, 1984*b*) may be regarded as quantitative.

A further challenging problem in PES is the accurate identification and subtraction of any background or other spurious signals that may be present. Scattered electron background is usually much more of a problem at lower photon energies (Fahlman *et al.* 1984*a*) in the near-threshold region, although background contributions and impurity lines may also arise in UPS and XPS if undispersed 'line' radiation is used as in the case for the XPS studies reported by Spears *et al.* (1974). Stray light and higher order radiation can also cause background problems, particularly in the use of monochromatised radiation from synchrotrons, storage rings or conventional light sources.

Intensities in photoionisation depend not only on the initial and final state overlap but also on the photon energy-dependent dipole matrix element (McCarthy 1985). The latter quantity changes rather rapidly with energy, especially at lower photon energies, as has been illustrated and discussed by Smid and Hansen (1984). Therefore, particularly at lower photon energies, the dipole matrix element must be accurately known in order to make any valid comparison between observed PES intensities and calculations of the pole strengths (i.e. the overlap) in satellite spectra. Calculations of photoionisation intensities at low photon energies are also difficult because the target induced distortion of the continuum wavefunction precludes a simple plane wave representation. On the other hand, at the higher photon energies, corresponding to XPS experiments, the dipole matrix element is effectively constant (Smid and

Hansen 1984) over the small energy range involved in the satellite spectrum, and XPS results should therefore be more directly comparable with calculations, if the measurements are at the magic angle and also transmission corrected. However, it should also be noted that the high photon energies of 1200–1500 eV typically used in XPS measurements correspond to valence shell electron momenta of the order of 10 a.u. Thus any theoretical calculation of intensities at such high energies (i.e. electron momenta) should also take into account the consequent significant distortion of the electron waves as well as relativistic effects. In view of these various considerations, intermediate photon energies of 100–300 eV may be the best compromise for obtaining PES data suitable for comparison with theory.

An alternative technique for quantitative measurements of binding energy spectra, and one that has been extensively used to study noble gas *n*s satellite spectra, is binary (e, 2e) spectroscopy (McCarthy and Weigold 1976; Hood *et al.* 1977; Weigold and McCarthy 1978; Leung and Brion 1983; Weigold 1984; Cook *et al.* 1986) which is now increasingly known as electron momentum spectroscopy (EMS). EMS involves complete kinematic determination of an (e, 2e) ionising collision using fast electron impact with coincident detection of the two outgoing electrons. In the most commonly used symmetric non-coplanar geometry the two outgoing electrons are of fixed, equal, high energies and therefore no electron transmission corrections are required. At the high impact energies ($\gtrsim$ 1000 eV) used in EMS experiments, plane waves can be used to describe the incoming and outgoing electrons. It is also important to note that EMS samples the low momentum part of the (ionised) electron wavefunction and therefore distortion effects are negligible, at least below momenta p of $\sim 1 \cdot 5$ a.u. (McCarthy and Weigold 1985; Cook *et al.* 1986). Furthermore, the coincidence detection used in EMS automatically eliminates non-spectral backgrounds as well as any double scattering events which can in some cases influence PES experiments. In addition, the fact that EMS can also determine orbital electron momentum distributions, i.e. $\psi^2(p)$, means that the initial state orbital signature of satellite structure, as for example in the noble gases (McCarthy and Weigold 1976; Leung and Brion 1983), can be determined directly. Further useful features of EMS are that there are no complicating terms such as the (photon energy-dependent) dipole matrix element or the angular distribution parameter β, both of which influence intensities observed in PES measurements. Therefore the binding energy spectrum intensities observed in EMS for a given symmetry manifold are expected to be directly proportional to the actual pole strengths (overlap) (Cook *et al.* 1981; McCarthy 1985) provided that the plane wave impulse approximation (PWIA) is valid (McCarthy and Weigold 1976, 1985; Cook *et al.* 1986). The conditions for the PWIA to be obeyed are fulfilled if the incoming and both outgoing electron energies are sufficiently high (typically the impact energy must be at least 1000 eV for valence shell processes). The quantitative validity of the PWIA below $p \sim 1 \cdot 5$ a.u., as well as that of the distorted wave (DWIA) treatment at higher momenta, has been convincingly demonstrated in recent EMS experiments on main and satellite lines for argon 3p and 3s ionisation (McCarthy and Weigold 1985) and even more directly for xenon 5p and 5s ionisation (Cook *et al.* 1986). Thus EMS satellite intensities are most appropriate for direct comparison with calculated pole strengths or transition probabilities (Cook *et al.* 1980, 1981; McCarthy 1985). It should be noted that some (but not all) of the early binary (e, 2e) experiments, notably some of those on argon and xenon (McCarthy and Weigold 1976; Hood *et al.* 1977; Weigold and McCarthy 1978), were carried out at impact energies (400 eV) that were probably too low for complete validity of the PWIA and such results may therefore not permit valid comparison of satellite intensities with most calculations and/or high energy PES measurements. The relatively poor energy resolution used in some earlier measurements may also complicate intensity interpretations where there are closely spaced states.

In a recent theoretical article, McCarthy (1985) has explored the relationship between satellite intensities (within a given symmetry manifold) in PES and EMS. In the absence of ground state correlations, the relative intensities in EMS are expected to be similar (at least up to a certain momentum) to those in the higher photon energy (XPS) regime (where photon energy effects due to the dipole matrix element should be minimal). Similar ideas have recently been discussed for argon by Mitroy *et al.* (1985) as well as earlier by Cook *et al.* (1981) in the case of the COS molecule for which a variety of types of binding energy spectra [EMS, XPS and dipole (e, 2e)*] were compared with many-body Green's function calculations. Likewise a more recent EMS study of the inner valence region of binding energy spectra of CO_2, COS and CS_2 (Leung and Brion 1985) shows a close similarity with corresponding XPS intensities (Allan *et al.* 1972) as well as those predicted by molecular many-body calculations (Schirmer *et al.* 1979; Cook *et al.* 1981; Nakatsuji 1983).

In view of the diversity of many-body calculations of *molecular* photoionisation (von Niessen *et al.* 1984; Cederbaum *et al.* 1986), it is surprising to find that there have been comparatively few attempts at high level calculations of binding energy spectra for more fundamental, and presumably more tractable, systems such as the noble gas atoms. However, CI calculations for noble gas *n*s ionisation have been reported by Dyall and Larkins (1982*a*, 1982*b*), Hansen and coworkers (Hansen 1982; Hansen and Persson 1978; Smid and Hansen 1981, 1983–5) and also by Mitroy *et al.* (1984). In the case of the argon $3s^{-1}$ spectrum, the calculations by Dyall and Larkins and also those by Hansen and coworkers are in fair agreement with the XPS intensities reported by Spears *et al.* (1974), although they are in significant disagreement with the satellite intensities reported in both earlier EMS measurements (McCarthy and Weigold 1976; Weigold and McCarthy 1978) and more recent measurements (Leung and Brion 1983; McCarthy and Weigold 1985). However, in contrast, these EMS results are reasonably well reproduced by the recent calculations reported by Mitroy *et al.* (1984). For xenon, the $5s^{-1}$ spectrum relative intensities in EMS (Leung and Brion 1983; Weigold 1984; Cook *et al.* 1986) and XPS (Spears *et al.* 1974; Gelius 1974) at $h\nu = 1487$ eV [but not at 1254 eV (Spears *et al.* 1974)] are in semi-quantitative agreement with each other, although it should be remembered that both sets of XPS measurements were made at an ejection angle of 90° rather than at the magic angle. The calculations for Xe $5s^{-1}$ by Hansen and Persson (1984) are in fair agreement with the XPS and the more recent EMS measurements except in the case of the XPS data at 1254 eV (Spears *et al.* 1974).

On the basis of their calculated satellite intensities for the Ar $3s^{-1}$ spectrum and a very few UPS (Adam *et al.* 1978*a*, 1985) and XPS (Spears *et al.* 1974) data points [of

* An alternative method of measuring binding energy spectra throughout the valence region, at modest energy resolution, is dipole (e, 2e) spectroscopy (Brion and Hamnett 1981; Brion 1985) which provides a *quantitative* simulation of tuneable energy PES. It should be noted that the fast electron impact method of dipole (e, 2e) spectroscopy is quite distinct from binary (e, 2e) (i.e. EMS) since dipole (e, 2e) employs completely different kinematics and involves negligible momentum *transfer*.

which the accuracy of the XPS data is seriously in question (Mitroy *et al.* 1985; Brion *et al.* 1986)], Smid and Hansen (1984) have predicted that the ratio of satellite to main line intensity in the Ar $3s^{-1}$ spectrum should *increase* with a *decrease in photon energy*. By inference they also predicted the same trend for Kr $4s^{-1}$ and Xe $5s^{-1}$ satellite spectra, although it should be noted that Adam *et al.* (1978*b*) had earlier suggested the reverse was true for Xe $5s^{-1}$ spectra on the basis of magic angle PES measurements over a limited photon energy range. Furthermore, since their calculated intensities and the measured XPS intensities (Spears *et al.* 1974) for Ar $3s^{-1}$ were in reasonable agreement with each other but in significant disagreement with results of EMS, Smid and Hansen have also repeatedly suggested (Hansen 1982; Smid and Hansen 1981, 1983, 1984) that this may indicate inadequacies in the PWIA model used to interpret EMS [i.e. binary (e, 2e)] measurements. It is of great importance to further investigate these questions, in view of the rapidly developing use and apparently powerful potential for EMS in experimental quantum chemistry (Bawagan *et al.* 1985; Brion 1986) and in particular for estimating CI coefficients (McCarthy and Weigold 1985; Cook *et al.* 1986) and detailed wavefunction evaluation at and beyond the Hartree–Fock model (Bawagan *et al.* 1986). However, it should be noted that the very recent detailed experimental and theoretical studies of argon (McCarthy and Weigold 1985) and xenon (Cook *et al.* 1986) have provided further convincing evidence of the validity of the PWIA model as used in EMS. Nevertheless the apparent inconsistency of EMS results with calculations and also XPS measurements prompts further investigation of the situation.

In the meantime, Mitroy *et al.* (1985) have drawn further attention to this confusing situation and explicitly suggested that the XPS experiments by Spears *et al.* (1974) for Ar $3s^{-1}$ may be subject to large and indeterminate backgrounds (even a simple visual examination of their XPS spectra indicates large and often sloping backgrounds, as well as broad features not observed in other work). If this is the case and the XPS intensities reported by Spears *et al.* are incorrect, then the calculations for Ar $3s^{-1}$ by Smid and Hansen (1981, 1983, 1984) may also be inadequate, as inferred by Mitroy *et al.* (1985). A further complication is that the XPS spectra of both Ar and Xe reported by Spears *et al.* (1974) and also by Gelius (1974) were determined at 90° instead of the magic angle. Since the β values for satellites in some cases may be both state and energy dependent ($\beta = 2$ only for a pure *n*s electron), this would require an increase in the measured satellite to main line relative intensities in order to give true (magic angle) values, as has been discussed by Fahlmann *et al.* (1984*a*). Further complications in comparisons of calculated and measured satellite intensities may also occur because:

(i) Any differences in energy resolution in the various PES and EMS experiments may affect relative peak heights and result in different band shapes if there are many closely spaced final ion states (satellites). As a result, intensities in general should be compared on an area rather than a peak height basis.

(ii) Different PES and EMS experiments exclude or include different amounts of the double ionisation continua ($ns^2\,np^4\epsilon d$) due to 'cutoff' by the high binding energy limit of the spectral range studied. Tables and spectra in the various experimental studies must be carefully examined to ascertain those portions of the spectra which have been included and those which have not been included. For this reason, relative intensities are preferred to the use of spectroscopic factors.

(iii) Some early EMS experiments were carried out at low impact energies (e.g. 400 eV) where the PWIA may not be well obeyed and as a result satellite relative intensities may be different from those expected on the basis of the PWIA. It is now known that impact energies of at least 1000 eV are needed to satisfy the PWIA for valence shell ionisation.

In view of the confused situation involving the diverse opinions and conflicting evidence in the literature as discussed above, and because magic angle PES measurements have not been reported at photon energies above ~ 80 eV, we have attempted to clarify the situation by carrying out new PES experiments for argon and xenon over a range of higher photon energies using synchrotron radiation. The distribution of satellite intensity is investigated as a function of photon energy up to 130 eV. In addition, comparison of these new PES measurements with recently published higher quality EMS data, obtained at high impact energies and better resolution than earlier work, provides further insight into the comparison of EMS and high energy PES as well as to the validity of the approximations used to interpret binary (e, 2e) (i.e. EMS) experiments. Brion *et al.* (1986) have already briefly reported on preliminary results for Ar $3s^{-1}$ photoionisation. More comprehensive results for argon as well as new measurements for xenon are now presented. The results are also compared with the various theoretical predictions.

2. Experimental

Photoelectron spectra have been obtained for gaseous argon ($n = 3$) and xenon ($n = 5$) in the region of the valence shell ns^{-1} photoionisation over the photon energy range 60–130 eV.* The measurements were made using a Leybold Heraeus LHS-11 hemispherical electron spectrometer mounted at the magic angle with respect to the photon polarisation vector (Yates *et al.* 1985). The polarised photon source used was the continuum from the 220 MeV Tantalus I storage ring at the Synchrotron Radiation Center of the University of Wisconsin. The radiation was monochromatised using the Mark IV Grasshopper grazing-incidence UHV monochromator (Tan *et al.* 1982) installed on the Tantalus beam line which constitutes the Canadian Synchrotron Radiation Facility (CSRF). For most of the spectra, the monochromator slit widths were selected at each photon energy to provide a monochromator/photoelectron spectrometer combined band pass in the range $1 \cdot 7 \pm 0 \cdot 1$ eV FWHM. This resolution was chosen in order to facilitate direct comparison of the PES spectra with recent EMS spectra (Leung and Brion 1983; Weigold 1984; McCarthy and Weigold 1985) as well as earlier XPS data (Spears *et al.* 1974) obtained at comparable energy resolution. Some spectra were also obtained at different resolutions to investigate the effect of resolution on band shape and peak height and also to establish consistency with earlier high resolution PES work. The electron spectrometer was operated at a constant pass energy of 50 eV and under these conditions the electron transmission function is known to be effectively constant (Yates *et al.* 1985) over the range of electron kinetic energies involved in the present work. Gas samples (Matheson lecture bottles) were leaked into the interaction region via a multichannel jet.

Typical instrumental performance is illustrated by the spectra shown in Figs 1*a* and 2*a*. Fig. 1*a* shows the Ar $3s^{-1}$ binding energy spectrum in the 26–50 eV region

* The value 130 eV represents the practical upper limit of monochromatised photon energies for PES on the Tantalus I storage ring.

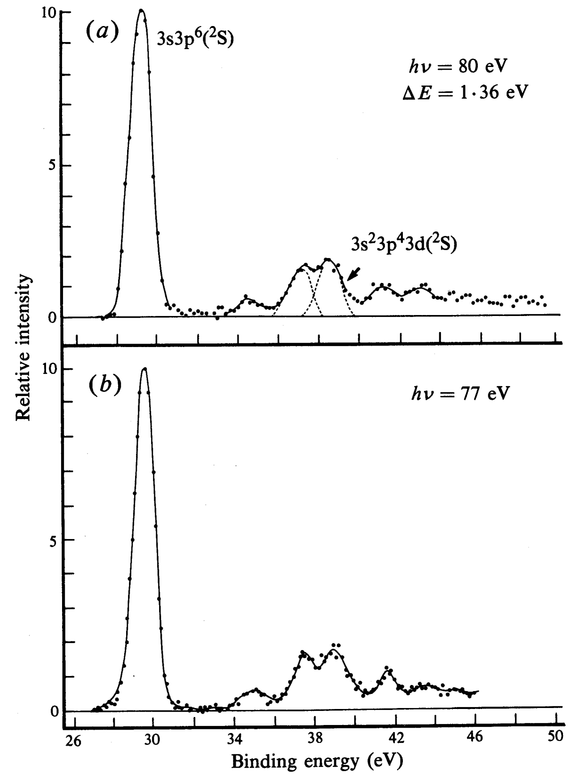

Fig. 1. Ar $3s^{-1}$ magic angle photoelectron spectra from (*a*) the present work at $h\nu = 80$ eV; (*b*) Adam *et al.* (1978*a*) at $h\nu = 77$ eV.

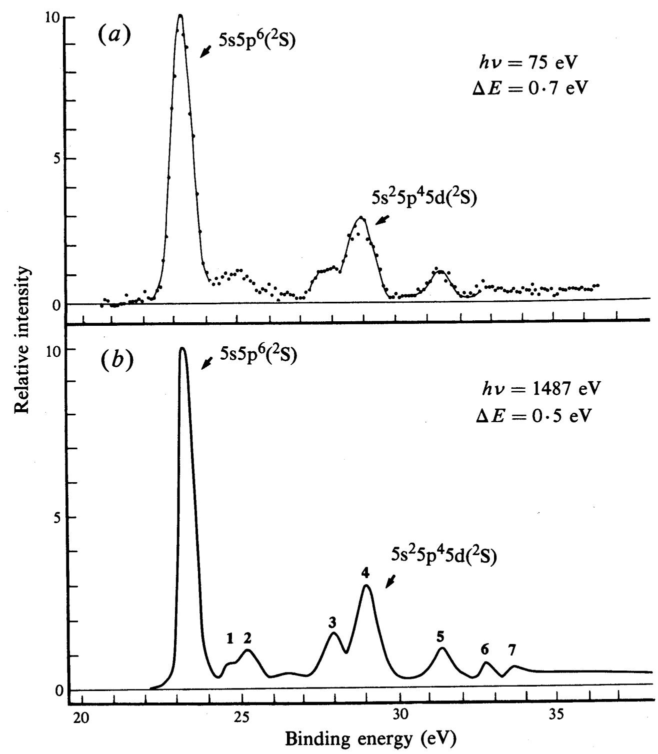

Fig. 2. Xe $5s^{-1}$ photoelectron spectra from (*a*) present work, magic angle spectrum at $h\nu = 75$ eV; (*b*) Gelius (1974), 90° spectrum at $h\nu = 1487$ eV.

obtained at a photon energy of 80 eV and $\Delta E = 1\cdot36$ eV FWHM resolution. This result is entirely consistent with the $h\nu = 77$ eV spectrum (Fig. 1*b*) obtained under essentially similar conditions by Adam *et al.* (1978*a*). Detailed interpretation and spectral assignment of the Ar $3s^{-1}$ spectrum has previously been presented (Adam *et al.* 1978*a*, 1985; Fahlman *et al.* 1984*a*; McCarthy and Weigold 1985; Smid and Hansen 1983) and will not be discussed further in the present work which is primarily concerned with intensities. Similarly Fig. 2*a* shows the presently obtained magic angle Xe $5s^{-1}$ spectrum at $h\nu = 75$ eV and $\Delta E = 0\cdot7$ eV FWHM compared with the slightly higher resolution ($\Delta E = 0\cdot5$ eV FWHM) XPS spectrum (Fig. 2*b*) obtained at 90° by Gelius (1974) using monochromatised Mg Kα radiation (1487 eV). Although there are differences in relative intensity due to the small difference in resolution and the wide disparity in photon energies (see discussion below) the envelopes of spectral states are rather similar in the two spectra. This contrasts markedly with the spectral envelope observed nearer threshold (Fahlman *et al.* 1984*a*) with much lower photon energies. The relative intensities in the Xe 5s XPS spectrum reported by Gelius (1974) will be further discussed below and compared with EMS data as well as with the PES spectra obtained in the present work. Spectral interpretation and assignments for the Xe $5s^{-1}$ spectrum have been discussed previously (Adam *et al.* 1978*b*, 1979; Hansen and Persson 1984; Weigold 1984; Cook *et al.* 1986).

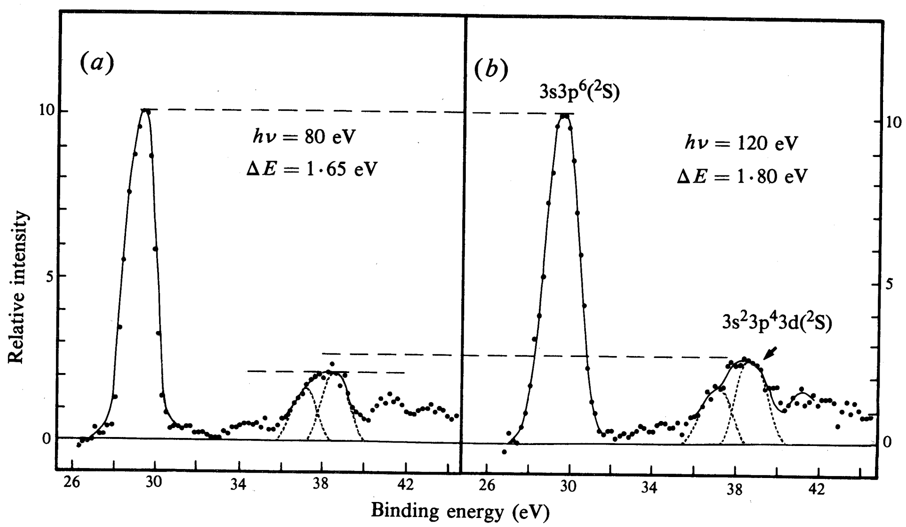

Fig. 3. Ar $3s^{-1}$ magic angle photoelectron spectra at (*a*) $h\nu = 80$ eV; (*b*) $h\nu = 120$ eV.

3. Results and Discussion

(a) Argon $3s^{-1}$ Spectra

Binding energy spectra were obtained for argon at photon energies of 80, 90, 100, 110, 120 and 130 eV, at an energy resolution in the range $1\cdot7\pm0\cdot1$ eV FWHM and over the binding energy range 26–50 eV. The lower binding energy portions of two typical spectra at photon energies of 80 and 120 eV are shown in Figs 3*a* and 3*b* respectively. Statistics at photon energies of 120 eV are poorer than those at 80 eV due to the rapidly decreasing photon flux at higher photon energies in the 220 MeV Tantalus storage ring. Nevertheless it can be seen that the height of the peak at 38·6 eV [dominant configuration $3s^23p^43d(^2S)$] relative to that of the main $3s^{-1}$ line at 29·3 eV increases to a small but significant extent with photon energy (the same conclusion results from a consideration of peak areas and provides a cross-check needed because of the slight resolution differences—see the small increase in half-width in going from $h\nu$ = 80 to 120 eV). Since both the resolution and general spectral shape are similar at $h\nu$ = 80 and 120 eV, a direct comparison of peak heights as in Fig. 3 provides a simple and valid visual test for changes in relative intensity. It can be seen from Figs 1 and 3 that there is no effective overlapping contribution to the peak at 38·6 eV from the lower energy satellite at ~37 eV. The relative intensity of this satellite structure at ~37 eV, located on the low binding energy side of the $3s^23p^43d(^2S)$ peak at 38·6 eV, decreases with an increase in photon energy [see Figs 1 and 3 and also Adam *et al.* (1978*a*, 1985) and Spears *et al.* (1974)]. Likewise it is relatively small in EMS spectra (Leung and Brion 1983; McCarthy and Weigold 1985). In the present work attention is mainly focused on the relative intensities of the main $3s3p^6(^2S)$ peak at 29·3 eV, the principal satellite $3s^23p^43d(^2S)$ at 38·6 eV, and on the total satellite intensity from 35–50 eV (i.e. the sum of all satellites plus the portion of the Ar^{2+} continuum up to 50 eV).

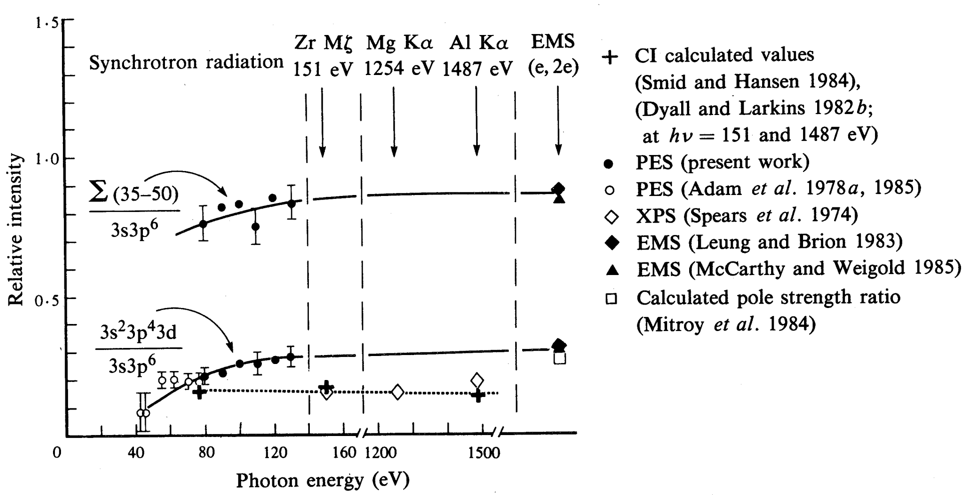

Fig. 4. Intensity ratios for satellite structure in the Ar $3s^{-1}$ photoelectron spectrum as a function of photon energy. The upper curve shows the ratio (peak areas) of the total satellite intensity (binding energy range 35–50 eV) to that of the main $3s3p^6$ hole state at 29·3 eV. The lower (solid) curve shows the ratio (peak height) of the $3s^23p^43d$ satellite line at 38·6 eV to that of the main $3s3p^6$ hole state at 29·3 eV. The dotted line shows the predicted trend from the CI calculated values.

In Fig. 4 the present Ar $3s^{-1}$ PES data are plotted (closed circles) as a function of photon energy in two ways: (i) the upper curve shows the ratio of the summed intensities (area) of the total satellite and continuum up to 50 eV binding energy to that of the intensity (area) of the main $3s^{-1}$ line at 29·3 eV binding energy; (ii) the lower curve shows the intensity (peak height) ratio (for example, as shown in Fig. 3) for the main satellite $3s^23p^43d(^2S)$ relative to the $3s3p^6(^2S)$ state. Also shown on the lower curve are corresponding synchrotron radiation PES data (Adam *et al.* 1978*a*, 1985) at lower photon energies from 77 eV down to $\sim$40 eV (open circles). The XPS results (Spears *et al.* 1974) at 151, 1254 and 1487 eV are also shown (open diamonds). The integral (upper curve) from 35–50 eV cannot be evaluated from the XPS data (Spears *et al.* 1974) owing to the uncertainty in the (sloping) background. In addition, data points (closed diamonds and triangles) are also shown from recent EMS spectra for Ar $3s^{-1}$ (Leung and Brion 1983;* McCarthy and Weigold 1985). These two, independent, high impact energy EMS experiments, carried out at similar energy resolutions, are in excellent quantitative agreement with each other and also give intensity ratios which appear to be in the region of the limit approached by the slowly increasing ratios observed in the present variable photon energy PES work, in both the upper and lower curves of Fig. 4. However, the XPS values (open diamonds Spears *et al.* 1974) are consistently lower and do not fit smoothly with the trend of the other data. Explanations for this discontinuity include the possibility that there is either some unknown photophysical effect occurring between the limit of the present photon data at 130 eV and the 151–1487 eV region, or that the interpreted relative spectral intensities reported for XPS (Spears *et al.* 1974) are either inappropriate due to the effects of β dependence caused by the 90° ejection angle and/or the reported intensities are incorrect. The latter possibility, strongly suggested by Mitroy *et al.* (1985) and further discussed by McCarthy and Weigold (1985) has been attributed to indeterminate backgrounds in the XPS spectra. Certainly an examination of all the XPS data (Spears *et al.* 1974) clearly indicates the possibility of large and often variable backgrounds, with the result that one would not expect to attain accurate intensities from the spectra. As will be seen in Section 3*b*, these conclusions are strongly further reinforced by a consideration of the presently obtained PES data for Xe $5s^{-1}$ together with published EMS data and a higher quality XPS spectrum of xenon (Gelius 1974) using a monochromatised Al Kα source.

It can be seen from Fig. 4 (lower plot) that the results (pluses) of the calculations by Smid and Hansen (1984) and also those by Dyall and Larkins (1982*b*) for the relative intensity of the $3s^23p^43d(^2S)$ state are well below the trend of the data projected from the present PES measurements in the range 80–130 eV and the value given by the two independent EMS experiments (Leung and Brion 1983; McCarthy and Weigold 1985). On the other hand, the ratio of 0·27 (open square) calculated by Mitroy *et al.* (1984) is in quite good agreement with the EMS and the present PES results. On the basis of the good agreement of their calculated values for argon with the XPS measurements (Spears *et al.* 1974) and the 58·3 and 77·2 eV UPS data points (Adam *et al.* 1978*a*, 1985), Smid and Hansen (1984) have predicted that the intensity of the $3s^23p^43d(^2S)$ satellite relative to the main $3s3p^6(^2S)$ line should *increase* with a *decrease* in photon energy (see dotted line representing this trend in Fig. 4). This prediction is clearly contrary to the trend of the present measurements between 80 and 130 eV and also to the projected behaviour towards higher photon energy. The present PES data agree well with low energy UPS measurements (Adam *et al.* 1978*a*, 1985) but are inconsistent with the XPS data (of questionable accuracy) of Spears *et al.* (1974).

* The EMS spectra reported by Leung and Brion (1983) have been integrated out to 50 eV. This was not evaluated in the original published work.

Based on the agreement of their calculations with the UPS and XPS data, Hansen (1982) and Smid and Hansen (1981, 1983, 1984) have also repeatedly questioned the validity of the approximations involved in the interpretation of intensities in EMS spectra. Consideration of the present new experimental PES work on argon, together with the calculations of Mitroy *et al.* (1984) and the questionable nature of the XPS intensities (Spears *et al.* 1974), leads to doubts not only as to the accuracy of the Smid and Hansen (1981, 1983–5) calculations and the predicted trend of intensity with photon energy but also to their resulting conclusions concerning the validity of the PWIA interpretation of intensities in binary (e, 2e) spectroscopy. These doubts are further supported by a consideration of the results for Xe 5s ionisation (see Section 3*b*), where the intensity *increase* with an *increase* in photon energy is much larger than that observed for argon and where, in addition, much more reasonable agreement is obtained with the better quality XPS measurements for Xe (Gelius 1974).

A direct comparison of the Ar $3s^{-1}$ binding energy spectra over the whole spectral range studied in the present PES work at $h\nu = 120$ eV and the recently reported EMS spectra (Leung and Brion 1983; McCarthy and Weigold 1985) is shown in Fig. 5. The PES and EMS spectral envelopes clearly exhibit similar shapes from threshold to the limit of the data in the Ar^{2+} continuum at $\sim$50 eV binding energy. Although small differences in spectral distribution appear to be present, particularly in the 32–37 eV region, the overall agreement is nevertheless seen to be quite good. However, it should be noted that the intensity distribution of these PES and EMS spectra is strongly at variance with that shown in the XPS spectrum (Spears *et al.* 1974). By $h\nu = 130$ eV the change of the energy dependent dipole matrix element over the binding energy range (due to the changing photoelectron energy) might be expected to be small (Smid and Hansen 1984). If indeed the spectral intensities of the XPS data (Spears *et al.* 1974) are spurious (Mitroy *et al.* 1985) then, again, it should be emphasised that any attempt to compare calculated intensities [such as those reported by Smid and Hansen (1981, 1984, 1985) and also by Dyall and Larkins (1982*b*)] with the XPS data of Spears *et al.* would be incorrect and any agreement and conclusions based thereon open to question. Certainly the trends of the present PES data and the EMS values cast serious doubts on the validity of a comparison of theory with the XPS data from Spears *et al.* (1974). As will be seen in the next subsection, the case of xenon is even more clear-cut, and a final assessment follows consideration of these results for Xe $5s^{-1}$ photoionisation.

(b) Xenon $5s^{-1}$ Spectra

Binding energy spectra were taken for Xe at photon energies of 60, 70, 75, 80, 90, 95, 100, 110, 115, 120 and 130 eV at an energy resolution in the range $1{\cdot}7 \pm 0{\cdot}1$ eV FWHM and over the binding energy range 18–40 eV. Typical spectra are shown in Fig. 6 (upper section). Similar to the case of argon it can be seen that the largest satellite peak, at $\sim 29{\cdot}0$ eV [containing several states of which the main intensity is considered to be a state with dominant configuration $5s^2 5p^4 5d(^2S)$ (Hansen and Persson 1984; Weigold 1984; Cook *et al.* 1986)] increases in height relative to the main $5s^{-1}$ line [dominant configuration $5s5p^6(^2S)$] at $\sim 23{\cdot}2$ eV. The relative contribution of the 29 eV peak changes from 22% to 58% as the photon energy changes from 60 to 130 eV (see also Fig. 7). The minor changes in energy resolution (Fig. 6) over this photon energy range are insufficient to affect this conclusion by more than a few per cent (see below). However, the case of xenon is slightly more complex than that for

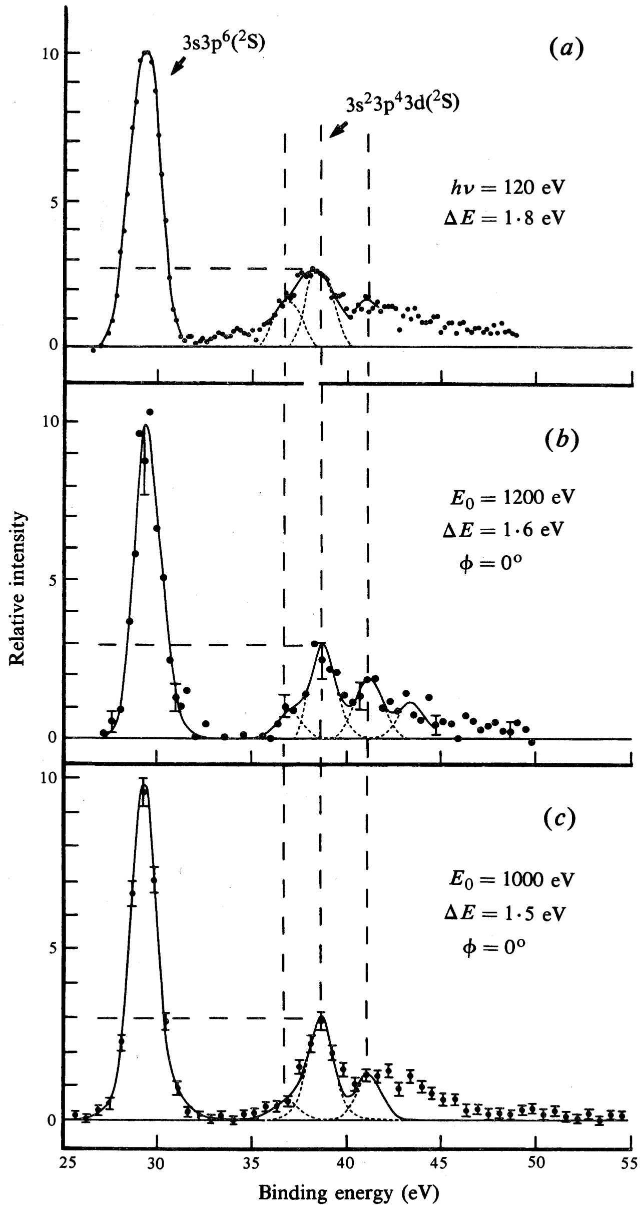

Fig. 5. Binding energy spectra in the Ar $3s^{-1}$ region for (*a*) PES at $h\nu = 120$ eV (present work); (*b*) EMS at $E_0 = 1200$ eV (Leung and Brion 1983); (*c*) EMS at $E_0 = 1000$ eV (McCarthy and Weigold 1985).

argon since, as shown in the XPS spectrum (Gelius 1974) reproduced in Fig. 2*b*, there are two closely spaced peaks (numbered 3 and 4) only 1·07 eV apart, and not separable at the energy resolution (1·5–1·7 eV FWHM) used for the PES spectra of Fig. 6 and the EMS spectra (Leung and Brion 1983; Weigold 1984) (see also Fig. 8).

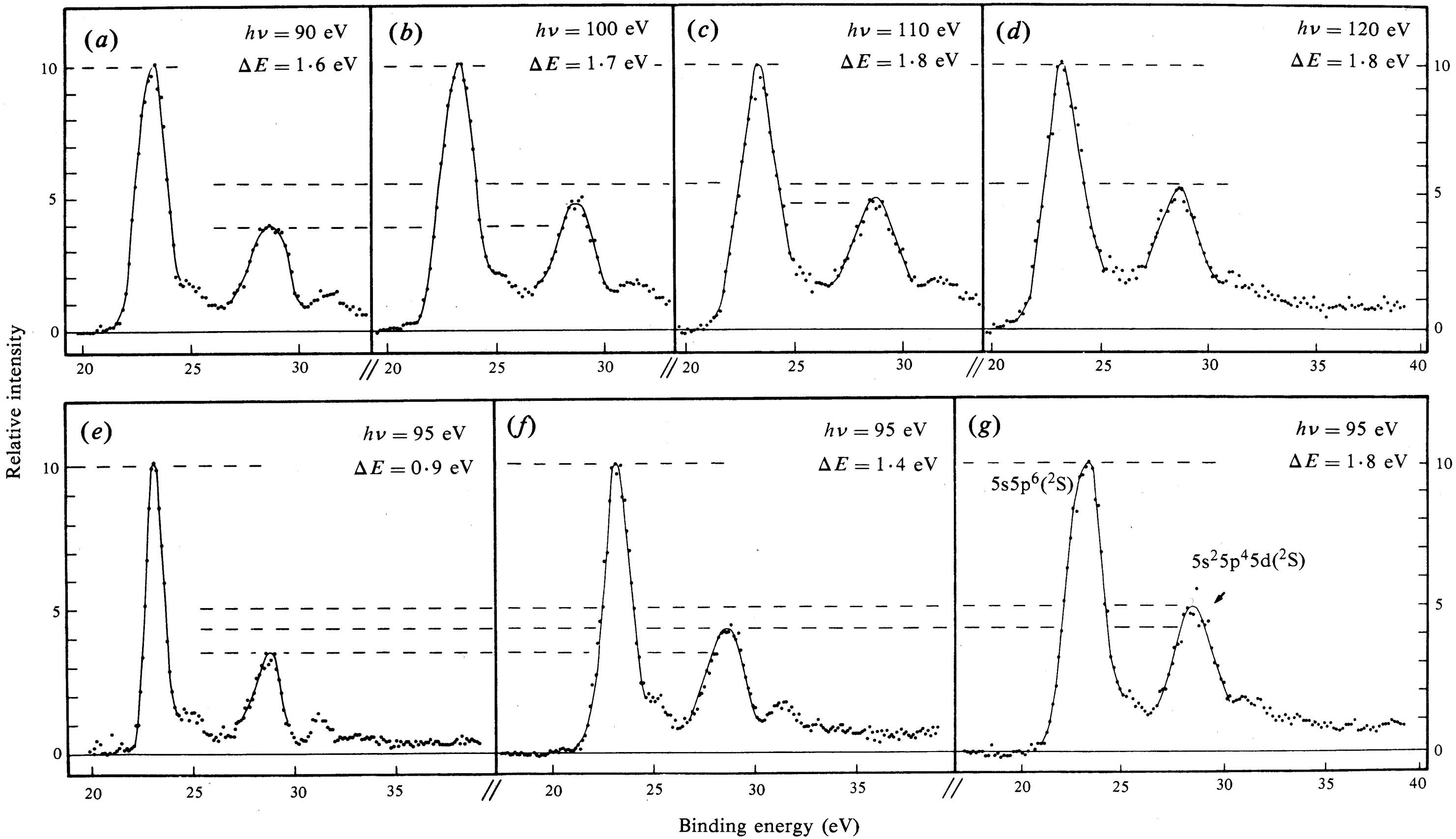

Fig. 6. Xe $5s^{-1}$ magic angle photoelectron spectra at the photon energies shown. Spectra (*e*)–(*g*) show the effect of a changing energy resolution on relative peak heights at $h\nu = 95$ eV.

As such, the observed peak shape and relative peak height in the 29 eV region will be quite strongly influenced by energy resolution, due to the resulting variation in overlap from contributions to the two peaks (3 and 4) at ~29 eV.

This resolution effect is clearly illustrated by the three Xe $5s^{-1}$ binding energy spectra shown in the lower section of Fig. 6 and obtained at a common photon energy of 95 eV with resolutions of 0·9, 1·4 and 1·8 eV FWHM respectively. The relative peak height at ~29 eV increases as expected with degradation in energy resolution (i.e. increase in ΔE). Therefore, in the case of Xe care must be exercised in comparing relative peak intensities from spectra obtained at substantially differing energy resolutions, particularly in the binding energy region of ~29 eV where there are likely to be many further unresolved states (Adam *et al.* 1978*b*). A careful examination of the 29 eV peak in the higher resolution PES spectrum (Fig. 2*a*) shows similar indications of fine structure, as has been reported by Adam *et al.* (1978*b*). Furthermore, as the resolution (ΔE) degrades significantly, increasing beyond the spacing of unresolved states, the peak *height* at ~29 eV will increase towards a value which would eventually reflect the sum of the intensities of peaks 3 and 4 in the higher resolution spectrum (see Figs 2*a* and 2*b*). A comparative examination of the spectra in Fig. 2 and Fig. 6*b* clearly shows this resolution/intensity effect to be the case. Any attempt to compare different resolution experimental intensity ratios of the type $5s^2 5p^4 5d(^2S)/5s5p^6(^2S)$ with each other or with theory must certainly take adequate account of these experimental considerations involving peaks 3 and 4. This is particularly important in comparing the higher resolution XPS spectrum reported by Gelius (1974) with the results of lower resolution EMS and PES spectra such as those discussed in the present paper, and this will be considered further here. A consideration of deconvoluted peak areas would avoid these pitfalls, but the presence of unresolved and probably unknown states prevents this and precludes direct comparison with calculations of intensities. It should be noted that area integration of the three spectra at 95 eV (Figs 6*e*–*g*) yields the same intensity ratio (regardless of resolution) within experimental error, for the total satellite intensity (26–38 eV) relative to that of the spectrum below 26 eV (the small contribution from peaks 1 and 2 in Fig. 2*b* has been included with the main line intensity for this area comparison).

Presently measured ratios of total satellite intensity (26–40 eV) to that of the main $5s^{-1}$ line, on an area basis, are shown in the upper curve of Fig. 7, with the lower curve giving the ratios for the peak height of the ~29 eV feature relative to that of the main line at ~23 eV.* Both ratios increase appreciably with an increase in photon energy over the range 60–130 eV. Considering first the (peak height) data on the lower curve, excellent agreement is found with corresponding data in the photon energy range below 80 eV taken from the work of Fahlman *et al.* (1984*a*) and also the earlier work of Adam *et al.* (1978*b*). The steep increase in the ratio occurring below ~50 eV is due to changing satellite intensities in the region of the well known valence shell Cooper minimum in xenon, an effect that has been investigated in detail by Fahlman *et al.* (1984*a*). Also shown in Fig. 7 are XPS values from the work of Spears *et al.* (1974) and Gelius (1974), as well as ratios derived from recent EMS

* The intensity corresponding to the main $5s^{-1}$ line in the present work, when computed on an *area* basis, also includes contributions from the relatively weak peaks (numbered 1 and 2 in Fig. 2*b*) which are unresolved at $\Delta E \sim 1{\cdot}7$ eV FWHM. The peak *height* of the main line at ~23 eV should, however, not contain any contribution from peaks 1 and 2, even at $\Delta E = 1{\cdot}7 \pm 0{\cdot}1$ eV FWHM.

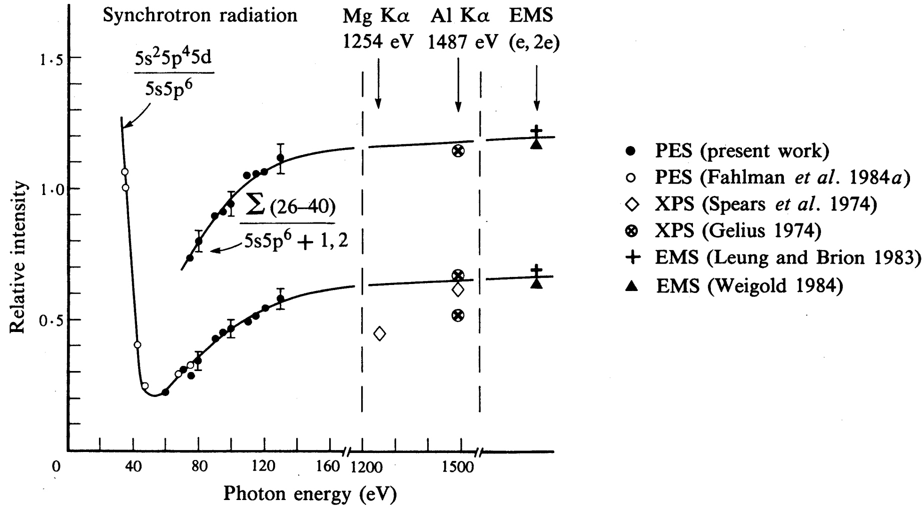

Fig. 7. Intensity ratios for satellite structure in the Xe $5s^{-1}$ photoelectron spectrum as a function of photon energy. The upper curve shows the ratio (peak areas) of the total satellite intensity (binding energy range 26–40 eV) to that of the main $5s5p^6$ hole state at 23·4 eV (plus the small contribution from peaks 1 and 2, see Fig. 2*b*). The lower curve shows the ratio (peak height) of the $5s^25p^45d$ satellite line at 29·1 eV to that of the main $5s^25p^6$ hole state at 23·4 eV. On the lower curve, the Gelius (1974) value (lower circled cross) has been corrected for estimated overlap from peak 3 (see text) to give the higher value shown.

measurements by Leung and Brion (1983) and by Weigold (1984). The present PES data clearly converge towards a value which is consistent with the corresponding ratio given by the EMS measurements (solid triangles and pluses). Considering first the (29 eV/23 eV) peak height ratios (lower curve) it can be seen that the Al Kα (1487 eV) XPS value (open diamond) reported by Spears *et al.* (1974) clearly lies on or close to the curve approaching the limiting value given by EMS, whereas the Mg Kα (1254 eV) point is clearly far below the trend of the other values. This may be due to uncertainties in the quantitative interpretation of the data from Spears *et al.* (1974), particularly at 1254 eV, as discussed above in the case of argon. These values could possibly be slightly raised by consideration of angular distribution effects since the measurements were made at 90° rather than at the magic angle. On the other hand, the high resolution Al Kα spectrum (Gelius 1974) gives a value of 0·52 for the ratio of peak 4 to the main line (see Fig. 2*b*) which lies somewhat below the trend suggested by the other data. However, this is not a valid comparison with the present data obtained at a resolution of 1·7±0·1 eV FWHM since (unresolved) peak 3 would contribute a small amount to the observed peak height at 29 eV. If the appropriate intensities reported by Gelius (1974) are considered in this fashion, it is estimated that the effective ratio at $\Delta E = 1 \cdot 7$ eV would rise to a value of ~0·65 (assuming a 50% contribution overlapping from peak 3). This revised value of 0·65 from the XPS data (Gelius 1974) is then clearly consistent with the other lower resolution experimental data, fitting smoothly between the present PES results and the limiting EMS values (0·67). Correction (if needed) of the Gelius (1974) 90° XPS data for angular distribution effects would also tend to increase the satellite intensities relative to the main line as has been discussed by Fahlman *et al.* (1984*a*). The close consistency of the 'corrected' Gelius data and also the Spears *et al.* (1974) 1487 eV XPS data point with the trend between the present PES work and the EMS results (Leung and Brion 1983; Weigold 1984) lends support to the expectation (Cook *et al.* 1981; McCarthy 1985) that high energy PES (i.e. XPS) and EMS should give similar distributions of satellite intensities within a given symmetry manifold.

We turn now to a consideration of the ratio of total satellite intensity (including continuum contribution) relative to that of the main transition (Fig. 7, upper curve). It can be seen that the ratio of the spectral area (26–40 eV) to that of the $5s^{-1}$ peak (plus the small contribution from unresolved peaks 1 and 2—see discussion above and Fig. 2) likewise shows a smooth progression with an increase in photon energy and appears to converge towards the limit given by the EMS data. In this case the equivalent *area* ratio (1·15) obtained from the Gelius (1974) XPS spectrum (including a small extrapolation from 38–40 eV estimated for the nearly flat continuum—see Fig. 2*b*) is reasonably consistent with the trend of the data and the limiting EMS values (1·2). Furthermore, any correction for angular distribution effects would also tend to raise this value, so again there is good consistency between the EMS values and the Gelius (1974) XPS data. It should be noted that the earlier Xe 5s EMS data reported by Weigold and McCarthy (1978) and by Hood *et al.* (1977) were obtained at impact energies of only 400 eV where it is now considered that the plane wave impulse approximation may be invalid, especially for a target as heavy as xenon, and therefore the relative intensities would not be expected to have reached their limiting values. This situation has doubtless complicated some of the earlier comparisons between EMS, PES and calculated intensities. The more recent EMS spectra (Leung and Brion 1983; Weigold 1984; Cook *et al.* 1986) were measured at higher impact energies of 1000–1200 eV and the intensities are in mutual good agreement. It is thus clear that the limiting values of relative satellite intensities have been effectively reached by or before 1000 eV impact energy.

Clearly satellite intensities strongly increase relative to that of the main $5s^{-1}$ line in xenon photoionisation as the photon energy increases. This is consistent with the earlier suggestions of Adam *et al.* (1978*b*) based on measurements at photon energies of 75·5 and 87·7 eV. The observed increase in relative satellite intensity with increase in photon energy is, however, contrary to the predictions of Smid and Hansen (1984) based on CI calculations for the noble gases argon, krypton and xenon.

Hansen and Persson (1978) have calculated satellite intensities in the Xe $5s^{-1}$ satellite spectrum using a CI method in the limit of high photon energy and obtained results in only fair agreement with the XPS spectrum reported by Gelius (1974). Calculations by Dyall and Larkins (1982*b*) show less satisfactory agreement with experiment. It is likely that relativistic effects need to be considered for a target as heavy as xenon (Cook *et al.* 1986). Earlier work (Cook *et al.* 1984) has shown that relativistic theory is needed to adequately describe the $5p_{3/2}$ and $5p_{1/2}$ valence shell momentum distributions as measured by EMS.

In Fig. 8 the presently reported PES spectrum of Xe at 120 eV is compared with the recently obtained EMS spectra (Leung and Brion 1983; Weigold 1984) at comparable low energy resolutions. Similar EMS results at slightly higher energy resolution have been reported very recently by Cook *et al.* (1986). The spectral envelopes are generally quite similar for the PES and EMS spectra. This lends further support to the preceding conclusions and suggests that spectral intensities (within a given symmetry manifold) at the high energy photon limit will be similar to those measured by EMS.

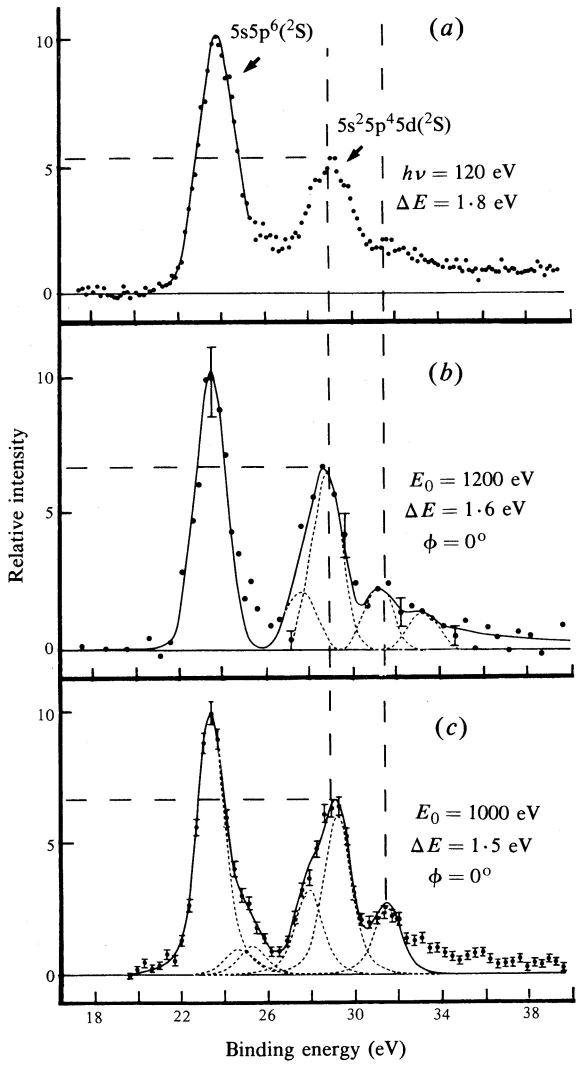

Fig. 8. Binding energy spectra in the Xe $5s^{-1}$ region for (*a*) PES at $h\nu = 120$ eV (present work); (*b*) EMS at $E_0 = 1200$ eV (Leung and Brion 1983); (*c*) EMS at $E_0 = 1000$ eV (Weigold 1984).

4. Conclusions

The presently obtained PES data for the Ar $3s^{-1}$ and Xe $5s^{-1}$ ionisation spectra clearly show an increase in satellite intensity relative to the main ns^{-1} line with an increase in photon energy at photon energies above the low energy region of Cooper minimum effects. This is the case for considerations of both the most intense satellite line and also for the total satellite plus continuum spectrum, up to the present limit of photon energy at 130 eV. This effect is even more prominent in xenon than in argon. In both cases the trend of the intensity ratios smoothly extrapolates towards the limiting values given by high impact energy electron momentum spectroscopy (EMS). The observed increase in relative satellite intensity with an increase in photon energy is contrary to the predictions of theoretical work by Smid and Hansen (1984). Observed intensities in the present Ar $3s^{-1}$ PES spectra are not well reproduced by any existing calculation of photoionisation. The findings of the present work strongly suggest the need for an even better theoretical understanding of the photoionisation process and improved calculations of photoelectron intensities. However, it is clear that the pole strength calculations for argon by Mitroy *et al.* (1984) show the best quantitative agreement thus far. The results and conclusions of the present study also contradict the conclusions (based on results of their calculations) of Hansen (1982) and Smid and Hansen (1981, 1983–5) suggesting that there may be difficulties in the interpretation of binary (e, 2e) experiments. The present results have been shown to be reasonably consistent with the high energy XPS data for Xe $5s^{-1}$ reported by Gelius (1974). However, the Ar $3s^{-1}$ XPS data reported by Spears *et al.* (1974), and also the Xe $5s^{-1}$ data at 1256 eV appear to be inconsistent with all the other experimental data, notwithstanding corrections for any unknown backgrounds or angular distribution effects. Unless there is some unknown and unexpected photophysical behaviour for Ar $3s^{-1}$ between 151 and 1487 eV photon energy (see Fig. 4), with a discontinuity between $h\nu = 130$ and 151 eV, it can only be concluded that the spectral intensities reported by Spears *et al.* (1974) are incorrect, as has been suggested recently by Mitroy *et al.* (1985). New magic angle XPS studies of Ar 3s and Xe 5s ionisation at photon energies above 130 eV would be helpful in resolving these questions.

The present work also emphasises the need for caution in interpreting relative spectral intensities from different experiments obtained under different conditions. Such considerations should be carefully taken into account, as should the contribution from Ar^{2+} and Xe^{2+} continua, in comparing theory and experiment. Due to the wide energy range of the continuum contribution, spectroscopic factors (i.e. relative intensities normalised to a total of unity according to the sum rule) are difficult to obtain with certainty, and intensities are therefore perhaps best reported on a relative basis compared to the main ns^{-1} line or to some other combinations of spectral features. Such a procedure also enables quantitative comparison of data from different sources, obtained over different energy ranges. Although the double ionisation continuum appears to converge rapidly at the higher binding energies (see Figs 5 and 8), the additional integrated intensity (i.e. above 50 eV for Ar, and above 40 eV for Xe) out to infinite binding energy may not be negligible. It is of interest, however, to note that recent preliminary calculations (I. E. McCarthy, personal communication, 1985) suggest rapid convergence of the double ionisation continuum such that most of the intensity has been included within the range of the present EMS experiments. An added problem in this regard is that an extended range of double ionisation can only be accurately measured by (e, 3e) or (ν, 2e) experiments (Yudin *et al.* 1985).

Finally it is also of importance to note that there is an intrinsic difference between high photon energy PES and EMS in that the former samples the high momentum part (3–10 a.u.) and the latter the low momentum part (0–2 a.u.) of the wavefunction.

This difference would not necessarily be expected to lead to differences in the relative satellite intensities within a given symmetry manifold. However, a very recent theoretical paper by Amusia and Kheifets (1985) expresses a contrary viewpoint and reports calculations of argon $3s^{-1}$ satellite intensities showing different spectroscopic factors for XPS and EMS based upon differences in the momentum transfer to the ion in each process. These calculations are in quite good agreement both with the respective XPS results for Ar $3s^{-1}$ reported by Spears *et al.* (1974) and also with the earlier EMS results for Ar $3s^{-1}$ reported by McCarthy and Weigold (1976). The theoretical findings of Amusia and Kheifets (1985) must, however, be treated with caution in view of the present PES experimental results and the other related considerations discussed above. Particularly troubling are the serious doubts indicated both here and elsewhere as to the quantitative accuracy of the Spears *et al.* (1974) XPS data for argon. Also, if the arguments of Amusia and Kheifets (1985) are correct, it is puzzling to understand why the better quality XPS data in the case of xenon (Gelius 1974) gives satellite intensities in reasonably close agreement with EMS. A further problem is that a plane wave description as used by Amusia and Kheifets (1985) for photoionisation calculations of XPS intensities is unlikely to be correct since distortion is expected at such high momenta. However, it is of interest to note that their calculations of the EMS intensities, where distortion should not be a problem, are in good agreement with experiment (Leung and Brion 1983; McCarthy and Weigold 1985). Amusia and Kheifets (1985) also claimed that EMS, rather than PES, gives correct spectroscopic factors. It is again evident that further theoretical work is needed as well as new high energy XPS measurements for argon.

The orbital electron momentum p corresponding to the EMS spectra (Leung and Brion 1983; Weigold 1984; McCarthy and Weigold 1985) is $\sim 0 \cdot 1$ a.u. under the conditions ($\phi = 0°$) of the spectra shown in Figs 5 and 8. In the case of the Xe $5s^{-1}$ spectrum, very recent EMS work (Cook *et al.* 1986) has shown that relative satellite intensities are independent of momentum in the range 0–1·5 a.u., which was the momentum range of the measurements. In contrast, at photon energies of 130 and 1487 eV, p is 2·7 and 10·4 a.u. respectively. The quite close agreement between relative intensities in the present PES work at 130 eV photon energy and the EMS data for both Ar and Xe, despite a difference of a factor of ~ 30 in the momenta, as well as the invarient Xe 5s EMS satellite relative intensity data in the momentum range 0–1·5 a.u., supports the general conclusions of the present study. While some of the much earlier reported EMS data were obtained under conditions where it is now known that limiting intensities may not be observed, the more recent EMS data at high impact energies clearly gives intensities reasonably consistent with the trend of those obtained at the higher intermediate photon energies used in the present PES work as well as with the high energy XPS data for Xe reported by Gelius (1974).

The results of the present study lend further support to the already large body of evidence, as summarised by McCarthy (1986), affirming the validity of the theoretical model used to interpret electron momentum spectroscopy.

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