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Electron impact excitation of argon and krypton: improved *r*-ratios

S Proctor[1] and M A Khakoo

Department of Physics, California State University, Fullerton, CA 92831, USA

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Abstract
New differential cross-section ratios (r) for electron impact excitation of the metastable states of argon and krypton are presented. The new measurements are taken with improved energy resolution and a novel moveable source method which yields overall better statistical errors than earlier measurements. These measurements were taken to check the accuracy of the r-ratios observed in the earlier experiments with argon (Khakoo *et al* 2004 *J. Phys. B: At. Mol. Opt. Phys.* **37** 247) which displayed significant deviations from the (statistical weight ratio) value of 5 at small scattering angles, and suggested the possibility of second-order effects in the electron impact excitation process. The measurements show that the r-ratios for argon stay close to the value of 5, in contrast to the earlier experiments, implying that second-order effects can be considered small. Additionally, new and similarly improved r-ratios for krypton were measured. These measurements reproduce the results of earlier measurements taken by our group which showed significant departures of r from the value of 5.

1. Introduction

The electron impact excitation of the ground ($\ldots ns^2np^6$ configuration) n^1S_0 state of a heavy noble gas (neon or above) to its first excited-electron $np^5(n+1)s$ configuration results in the excitation of four levels. The collective study of the excitation of these four levels constitutes a unique system where differential cross-sections (DCS, $d\sigma/d\Omega$) and their ratios provide valuable insights on relativistic interactions contributing to the electron scattering dynamics (Khakoo *et al* 1994, Guo *et al* 1999). In the single-configuration representation, these $\left|np^5(n+1)s[J_{\rm core}]^o_J\right\rangle$ levels can be expressed in the intermediate-coupling scheme

[1] Present address: Department of Mathematics, University of California, Riverside, CA 92521, USA.

(see e.g. Bartschat and Madison 1992) in terms of *LS*-coupling wavefunctions $|\phi\rangle$ as

$$\begin{aligned}
&\left|(n+1)\mathrm{s}[3/2]^{\mathrm{o}}_2\right\rangle = |(n+1)^3\mathrm{P}_2\rangle,\\
&\left|(n+1)\mathrm{s}[3/2]^{\mathrm{o}}_1\right\rangle = \alpha|(n+1)^3\mathrm{P}_1\rangle + \beta|(n+1)^1\mathrm{P}_1\rangle,\\
&\left|(n+1)\mathrm{s}'[1/2]^{\mathrm{o}}_0\right\rangle = |(n+1)^3\mathrm{P}_0\rangle \qquad \text{and}\\
&\left|(n+1)\mathrm{s}'[1/2]^{\mathrm{o}}_1\right\rangle = \alpha|(n+1)^1\mathrm{P}_1\rangle - \beta|(n+1)^3\mathrm{P}_1\rangle.
\end{aligned} \tag{1}$$

Here α and β are the intermediate-coupling (unitary) mixing coefficients (i.e., $\alpha^2 + \beta^2 = 1$). For a discussion of these see, e.g., Khakoo *et al* (1994).

Khakoo *et al* (1994), discuss three DCS ratios (r, r' and r'') between pairs of states given in equations (1). The ratio r is the DCS ratio of the metastable $J = 2$ and $J = 0$ levels:

$$r = \frac{\mathrm{DCS}\big((n+1)\mathrm{s}[3/2]^{\mathrm{o}}_2\big)}{\mathrm{DCS}\big((n+1)\mathrm{s}'[1/2]^{\mathrm{o}}_0\big)}. \tag{2}$$

In the case where relativistic (spin–orbit) interactions between the projectile and target electrons are small and where the energy dependence of the *T*-matrix operator is not affected by the energy splitting between the $J = 2$ and $J = 0$ levels (Bartschat and Madison 1992), r should be equal to the ratio of the statistical weights $(2J + 1)$ of these levels, which is 5. Relativistic (spin–orbit) interactions between the target (either the core, excited electron, or both) and the projectile electron would cause deviations of r from the value of 5. We point out here that the projectile electron relativistic spin–orbit coupling with the target core, resulting in angular momentum exchange, will vary significantly among the heavy noble gases since it depends on the tightness of the core coupling with itself.

This work was stimulated by the earlier r measurements for argon taken several times in this group (Khakoo *et al* 1994, 2004) and earlier by Chutjian and Cartwright (1981) that showed values close to 5 for large scattering angles, but surprising precipitous drops (falling to as low as 1) at small scattering angles (θ). In light of this, a possibility was suggested by Khakoo *et al* (1994) that second-order processes during the electron scattering process that involve coupling between the $J = 1$ levels to the metastable $J = 0, J = 2$ levels could populate these $J = 0, 2$ levels and result in a deviation of r from its statistical weight value of 5. Since this coupling is inversely proportional to the energy difference between the $J = 1$ and $J = 0, 2$ levels, an intuitive picture would indicate that the $J = 0$ level would gain in population since it is closer to the $\left|(n + 1)\mathrm{s}'[1/2]^{\mathrm{o}}_1\right\rangle$ level, which has the largest differential cross-section at small θ. This would be observed in second-order matrix elements in a perturbative theoretical model, or in a full close-coupling model if relativistic spin–orbit coupling interactions between the projectile electron and the target are included. This effect should be observed even in light targets which could be described by *LS* coupling as long as the presence of the projectile electron is able to effect significant coupling between the $\left|n\mathrm{p}^5(n+1)\mathrm{s}[J_{\mathrm{core}}]^0_J\right\rangle$ levels. However, it was also suspected that previous experimental data may have suffered from systematic errors that present themselves when unfolding electron energy loss spectra (i.e., resolving a composite energy loss spectrum into its individual line components using the method of linear least-squares, e.g., see, Khakoo *et al* (1994)). In addition, a careful re-investigation of r at small θ would need one to be able to make measurements with better statistics than the previous measurements of Khakoo *et al* (1994, 2004) and Chutjian and Cartwright (1981). Therefore, it was deemed important to verify the behaviour of r at small θ using better experimental techniques to look for these second-order effects.

Here we present the results of a recent experiment that measured the r-ratios for argon, in which relativistic interactions between the projectile and target are small (Khakoo *et al* 2004, Bartschat and Madison1992) and krypton in which relativistic interactions between the projectile and target are significant (Guo *et al* 1999, Bartschat and Madison 1992) to investigate the previously observed deviation of r from its *LS*-coupled value of 5. The experimental technique was improved by using an electron beam with a narrower energy spread than previously used to better separate the four $|np^5(n+1)s[J_{\rm core}]^{\rm o}_J\rangle$ levels. Since the higher resolution operation resulted in a reduction of incident electron beam current, the accumulated scattered counts obtainable from this weaker source of scattered electrons was increased by employing the recently developed moveable source method (Hughes *et al* 2003) as is explained below. The present results are compared to previous measurements and existing theoretical models.

2. Experiment

The set-up for this high-resolution spectrometer has been discussed previously (Khakoo *et al* 2002) so only a brief summary will be given here. The apparatus consisted of an electron energy-loss spectrometer with double hemispherical energy selectors in both the gun and the analyser sections as has been detailed in Guo *et al* (2000). The spectrometer was housed in a vacuum chamber that was pumped with a 12 inch diffusion pump. The base pressure of the vacuum chamber was $\approx 1 \times 10^{-7}$ Torr. Both the gun and the analyser sections were baked to $>120\,^{\circ}$C during the experiment to maintain the stable conditions necessary for taking electron energy-loss spectra over long periods. To reduce the earth magnetic field the vacuum chamber was shielded with a doubly layered high-permeability, low-field μ-metal shield and a high-field, low-permeability μ-metal shield to provide a magnetic field of <2 mG in the collision region (see Guo *et al* (2000) for details). A significant feature of this spectrometer is the reduction of 'wings' in the instrumental energy profile that is often seen in spectrometers with single hemispherical analysers (e.g., that used in Khakoo *et al* (1996)). This characteristic enabled us to more easily resolve the weak metastable energy-loss features from the stronger dipole-allowed transitions in Ar. However, in the extreme cases in which the dipole-allowed transitions dwarf the metastable features, as is the case at small scattering angles in the present experiments, it was found that the effect of these reduced wings was not negligible. The spectrometer operated at an energy resolution of 30–38 meV (full width at half maximum, FWHM) with an incident electron current ranging from 3 to 7 nA. The spectrometer could observe scattered electrons at scattering angles up to 130°. In the earlier measurements of r-ratios in the heavy noble gases, a well-tested multi-Gaussian unfolding program (Khakoo *et al* 1994) was used to unfold the spectra. The energy level values for argon and krypton used in the experiments were taken from Moore's spectroscopy tables (Moore 1952). Two significant improvements to the earlier spectral unfolding experiments were made

(a) Instead of the typical 40–50 meV energy resolution employed in the earlier work in argon (Khakoo *et al* 2004), the improved 30–38 meV resolution was obtained by using smaller apertures (0.7 mm diameter) to replace the existing apertures (1 mm diameter) in the electron gun. This resulted in a lower current of electrons (3–7 nA) as compared to $\approx$20 nA in the previous set-up.
(b) For each of the two energy-loss features, measurements were taken on resonance with the moveable source in and out of position to yield the net background subtracted counts. This method led to counting statistics which were about a factor of 4 better than for an equivalent experiment (without the moveable source; Hughes *et al* 2003) that scans the whole energy-loss spectrum and fits line profiles to the individual features.

With the above changes, we were able to improve upon our earlier statistical uncertainties while using an improved energy resolution. However, we have to accommodate for drifts

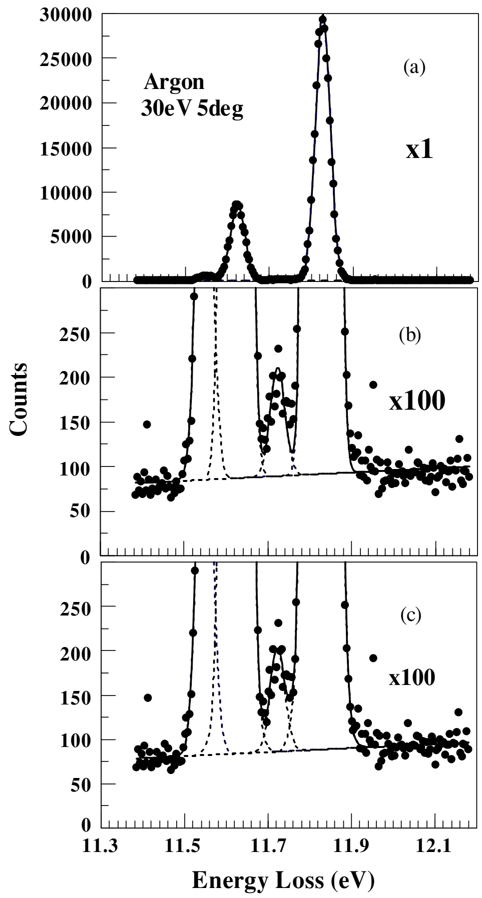

Figure 1. Plot qualitatively illustrating the effect of non-Gaussian line profiles on unfolding of argon spectra. Legend: ● data; — unfolding fit to spectrum; ...... individual line components. (a) Spectrum with single Gaussian fit. (b) Spectrum in (a) $\times 100$; (c) fit to the same spectrum with a line profile obtained from three Gaussians. Note: in (b), the fit does not follow the spectrum at the energy loss area around 11.75 eV as it does in (c). Also, the true line profile in (c) of the $|(n+1)s'[1/2]^{o}_{1}\rangle$ feature at 11.828 eV energy loss overlaps more with the weak $|(n+1)s'[1/2]^{o}_{0}\rangle$ feature next to it at 11.723 eV energy loss. Energy resolution here is 37 meV FWHM. At 44 meV, this overlap becomes markedly worse for unfolding. See text for discussion.

in the energy-loss scale (due to spectrometer power supplies' stability) during the moveable source experiment, which would affect r-ratios if neglected. In figure 1 we show a comparison between a single Gaussian unfolding of a small-θ argon energy loss (figure 1(b)) compared alongside a line profile closer representing the instrument's (figure 1(c)). As can be seen, at first view, it seems that the instrument's line profile follows closely those of the Gaussian (figure 1(a)), but in fact under magnification it is slightly, but significantly, broader at the wings (figures 1(b) and (c)). This will affect the unfolding at small θ when the metastable energy-loss features are dwarfed by the dipole-allowed features. At larger θ, the dipole-allowed features no longer dwarf the metastable features, so this effect is significantly reduced. Conservative estimates, based on such profiles observed in our experiment (for isolated transitions in helium), are to increase by a factor of ≈ 4 the effect of drift in energy loss on the variance of the r-ratios as compared to the sharper single Gaussian estimates. In figure 2 this is elaborated

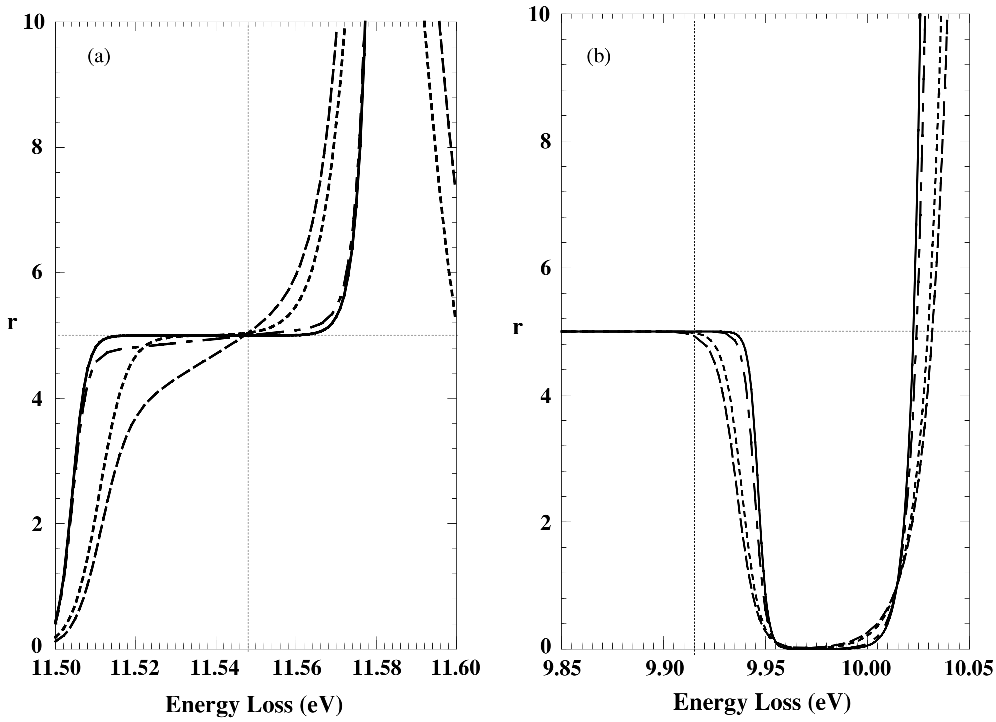

Figure 2. (a) Variation in measurement of r (assumed equal to 5) as a function of possible experimental drift in energy-loss value of the spectrometer, from its centred 11.548 eV energy-loss setting (the 0.175 eV jump from the $J = 2$ to $J = 0$ level energy loss was unaffected by drifts in our experiments), for argon at $E_0 = 20$ eV, $\theta = 5°$, using DCS values from Khakoo *et al* (2004). Legend: —— 32 meV FWHM single-Gaussian spectrometer line width; — - — - 32 meV FWHM experimentally derived multi-Gaussian linewidth; - - - - 44 meV FWHM single-Gaussian linewidth; — — — 44 meV FWHM experimentally derived multi-Gaussian linewidth. (b) Same as (a), but for krypton, with the spectrometer centred about the energy loss of 9.915 eV and jumping by 0.648 eV, for $E_0 = 20$ eV and $\theta = 5°$, using DCS values from Guo *et al* (2000). Legend is the same as (a).

further, where we show the effect of experimental energy-loss drift in the determination of r. In this calculation, using DCSs taken earlier in argon (Khakoo *et al* 2004) for $E_0 = 30$ eV and $\theta = 5°$, we see that for a 44 meV FWHM (single Gaussian line profile) a drift of 3 meV in the energy loss results in a change of $\approx$1.2% in r, whereas for a 32 meV resolution, a drift of 3 meV would produce a $\approx$0.2% effect. However, for the realistic case (non-Gaussian) of the line profile of our electron beam the effect of drift can be expected to be more than that for a single Gaussian. In figure 2(a) we show our estimates of the departure of r from 5 (assuming r was 5 in the first place) for practical profiles for argon taken at small θ. The results show a $>$3% deviation of r from 5 for a drift of 3 meV energy loss for a FWHM resolution of 44 meV, and a $\approx$0.8% deviation in r from 5 for a drift of 3 meV for a FWHM resolution of 32 meV. Hence, the effect of line wings is severe at small θ for argon where the dipole lines (hence their line-wings) dominate the dipole-forbidden lines. For krypton (figure 2(b)), we see the effect of drift is significantly smaller for tuning at or below the energy loss of 9.915 eV for the $J = 2$ state, being less than argon by a factor of $>$3. This is due to the lower DCS of the $\left|(n+1)\mathrm{s}'[1/2]^{\mathrm{o}}_1\right\rangle$ level as compared to the DCS of $\left|(n+1)\mathrm{s}[1/2]^{\mathrm{o}}_0\right\rangle$ level at similarly small θ, when compared to argon. The above observations show that it is possible to improve on the earlier measurements of r. Note that in all the above discussion we have not included the effect of drifts in the voltage of the power supply that jumps the energy loss from the $|(n+1)s[1/2]_2^o\rangle$ feature to the $|(n+1)s'[1/2]_0^o\rangle$ feature (0.175 V for argon and 0.648 V for krypton) because this supply voltage did not drift by more than 0.5 mV.

In the initial part of the experiment, a typical multi-channel energy-loss spectrum of the $|(n+1)s'[1/2]_1^o\rangle$ (at 11.825 eV for argon and 10.644 eV for krypton) feature was taken to establish the energy-loss scale to within ± 1 meV by fitting over the maximum of this feature. The energy loss was then offset to 11.548 eV for argon (9.915 eV for krypton), thus centring it on the $|(n+1)s[3/2]_2^o\rangle$ feature. Data were then accumulated for equal acquisition times with the energy loss centred at 11.548 eV (9.915 eV krypton) and 11.723 eV (10.563 eV krypton) which correspond to the $|(n+1)s[3/2]_2^o\rangle$ and $|(n+1)s'[1/2]_0^o\rangle$ features. While on each feature, the gas beam was modulated from the aligned position with the electron beam (ON) and out-of-alignment position from the electron beam (AWAY). Scattered electron counts were obtained for equal acquisition times for the two relevant features in both gas beam positions for a total of four measurements. Subtraction of the AWAY counts from the ON counts resulted in the background-free scattered counts for these two features from which r could be determined (see equation (2)). Drifts in these energy-loss values as monitored by a digital voltmeter did not exceed ± 2 meV during the experimental data acquisition times. Preliminary test r-ratios obtained at 32 meV resolution (FWHM) using the gas beam modulation method and using earlier conventional energy loss spectra taken at larger θ showed very good agreement between the two methods. These are displayed at the incident energy and scattering angle where this conventional analysis was undertaken.

3. Results and discussion

Our r-ratios for argon are plotted in figure 3 and for krypton in figure 4. In figure 3, we observe r-ratios that remain close to the value of 5 within experimental uncertainties, which are dominated by statistics. Other experimental errors (due to drifts in the electron and gas beam intensities) were negligible as was checked by performing the experiment only with the $|(n+1)s'[1/2]_1^o\rangle$ feature in both channels. Agreement with our earlier experimental r-ratios is excellent for $\theta > 30^\circ$ in all cases. However, at some energies, e.g., $E_0 = 17.5$ eV, 20 eV and 50 eV, our present r-ratios (which have significantly smaller uncertainties than the earlier r-ratios) do not show the previously observed decrease at small θ values. The reason for this is the fact that the earlier instrumental line profile of our spectrometer was probably not able to separate the dipole-allowed $|(n+1)s'[1/2]_1^o\rangle$ feature from the smaller neighbouring $|(n+1)s'[1/2]_0^o\rangle$ dipole-forbidden feature when the DCS ratio of these exceeded $\approx$20:1. With the improved resolution, the new experimental r-ratios remain close to 5 even when the dipole and metastable features were in a ratio of greater than 80:1. This is in excellent agreement with present theoretical calculations, of which several representative models are shown for comparison in the figures. Taking a weighted average of our new r-ratios gives at $E_0 = 15$ eV, 17.5 eV, 20 eV, 30 eV and 50 eV values of 5.03 ± 0.12, 5.30 ± 0.11, 4.92 ± 0.10, 4.87 ± 0.05 and 4.94 ± 0.11, respectively, with a total average r-ratio of 4.95 ± 0.04. The fact that r stays close to 5 shows that second-order effects in the scattering process are small for argon.

For krypton (see figure 4), r shows large deviations from 5. The present r-ratios are in very good agreement with our previous r-ratios and have significantly smaller uncertainties resulting in a more clearly defined shape of the r behaviour with θ, especially at intermediate θ around 60° to 90°. If second-order effects are small (as was concluded in the argon case),

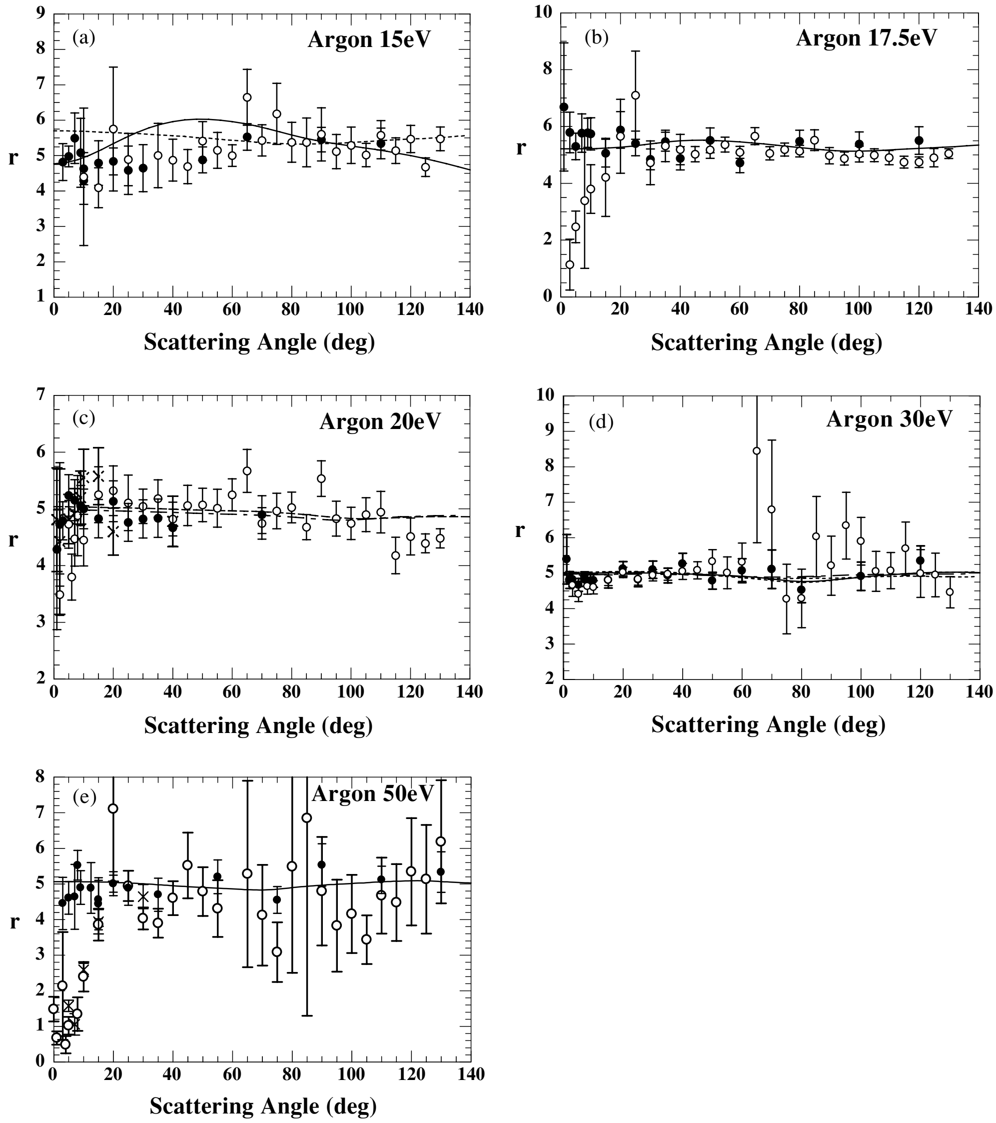

Figure 3. (a) r ratios for argon at $E_0 = 15$ eV. Legend: ● present r-ratios with moveable target method; ○ Khakoo *et al* (2004); —— 15-state R-matrix (Khakoo *et al* 2004); - - - - unitarized first-order many-body theory (Khakoo *et al* 2004). (b) Same as (a), but for $E_0 = 17.5$ eV. (c) Same as (a), but for $E_0 = 20$ eV. Legend is the same except: × present results with the electron spectrometer at high resolution (32–34 meV FWHM) and conventional unfolding of energy loss spectra; - - - - distorted-wave Born approximation (Khakoo *et al* 2004); — - — - relativistic distorted wave Born approximation with single configuration ground state wavefunctions (Khakoo *et al* 2004). (d) Same as (a) and (b), but for $E_0 = 30$ eV. All four models are plotted here. (e) Same as (a), but for $E_0 = 50$ eV. Legend includes: × present results with the spectrometer at a poorer resolution of 45 meV (FWHM) and conventional unfolding of energy loss spectra. The solid line is an average of all perturbative models, namely distorted-wave, relativistic distorted wave and unitarized first-order many-body theory.

the deviations of the krypton r-ratios from 5 indicate spin–orbit coupling in the continuum channel between the scattering electron and the target. The absence of its inclusion in

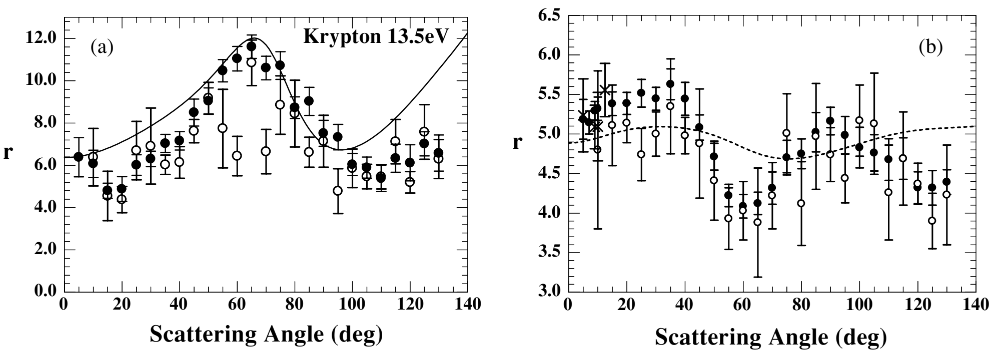

Figure 4. (a) Same as figure 3(a) but for krypton at $E_0 = 13.5$ eV and also: ○ Guo *et al* (2000) and —— 15-state *R*-matrix model, Guo *et al* (2000). (b) Same as (a), but for krypton at $E_0 =$ 20 eV. - - - - Unitarized first-order many-body theory, Guo *et al* (2000).

theoretical calculations gives the poorer agreement seen by all models to date of which the best representative (showing best agreement) is plotted for comparison. The significant increase of r around 60° to 90° is possibly due to interference between the direct and exchange scattering amplitudes, similar to Mott scattering spin–orbit effects (see, e.g., Kessler (1985)). It would be of great interest for a theoretical investigation to check this fact. This behaviour is in contrast to the results of Dümmler *et al* (1995) who measured left-right scattering asymmetries using spin polarized electrons (S_A) for the $J = 1$ levels of argon and krypton. Their results indicated that the spin–orbit interaction of the continuum electron was negligible in the scattering process for both argon and krypton, which showed a weak violation of *LS* coupling in both targets. Hence (incorporating Dümmler *et al*'s S_A results for the singlet states of krypton) one could conclude that spin–orbit effects are less prevalent for the dipole-allowed singlet states than for the triplet metastable states. In all the above cases, agreement with theory for argon is excellent (predominantly close to 5), but mixed for krypton.

4. Conclusions

We have used a novel moveable source technique coupled with conventional spectral acquisition methods to show clearly that for argon, the DCS ratio r stays close to the value of 5 even for small θ. This shows that the possibility of second-order effects is small. In addition, our results for krypton (where r significantly deviates from the value of 5) show that relativistic spin–orbit effects are more significant in the scattering process for excitation of the triplet (metastable) states investigated here than for the singlet (dipole-allowed) states investigated by Dümmler *et al* (1995). We also checked the earlier r-ratios taken by our group and found that they suffered from increased line profile effects at small θ which resulted in the erroneous dips observed at small θ.

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