

LETTER TO THE EDITOR

Differential cross section ratios for low-energy electron-impact excitation of the $4p^55s$ levels of krypton—sensitive tests of relativistic effects for heavy noble gases

Xuezhe Guo[†], M A Khakoo[†], D F Mathews[†], G Mikaelian[†], A Crowe[‡],
I Kanik[§], S Trajmar[§], V Zeman^{||}, K Bartschat[¶] and C J Fontes⁺

[†] Department of Physics, California State University, Fullerton, CA 92834, USA

[‡] Department of Physics, University of Newcastle, Newcastle-upon-Tyne NE1 7RU, UK

[§] Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA

^{||} Mathematics Department, University of Nottingham, Nottingham NG7 2RD, UK

[¶] Department of Physics and Astronomy, Drake University, Des Moines, IA 50311, USA

⁺ Applied Theoretical and Computational Physics Division, Los Alamos National Laboratory,
Los Alamos, NM 87545, USA

Received 24 November 1998, in final form 17 February 1999

Abstract. We present new experimental measurements and theoretical calculations of R -matrix and unitarized first-order many-body theory for electron-impact excitation of krypton. The usefulness of differential cross section ratios in providing sensitive tests of electron scattering models for the excitation of the $np^5(n+1)s$ configuration of the heavy rare gases is demonstrated. In addition to differential cross sections alone, these ratios provide interesting physical insights into the details of the collision process. Comparisons of the measured ratios with predictions from the present and other available calculations show some agreement, but also reveal that significant improvements of these models are required.

Electron-impact excitation of heavy rare gases is of current interest for several notable reasons. As more sophisticated collision models evolve, the experimental data required to test such theoretical methods must be very precise. The recently developed ‘convergent close-coupling’ (CCC) model has been applied to a range of light and heavy targets, such as H (Bray and Stelbovics 1992), Na (Bray 1994), He (Fursa and Bray 1997) and Ba (Trajmar *et al* 1998), but has been restricted to a non-relativistic formulation. A similar problem faces the newly developed ‘ R -matrix with pseudo-states method’ (RMPS) of Bartschat *et al* (1996). Although the RMPS was also used successfully in many non-relativistic applications (see, for example, Hudson *et al* 1996, Bartschat *et al* 1997, Bartschat 1998a, b and references therein), the number of coupled channels in relativistic calculations would rise quickly to a prohibitive level for most current serial computers.

However, a standard semi-relativistic R -matrix (RM) code is already in place (Berrington *et al* 1995). It handles the most important relativistic effects through the one-electron terms of the Breit–Pauli Hamiltonian. Recently, a 31-state model (RM31) was moderately successful in predicting the polarization of the light emitted after impact excitation of Ne, Ar, Kr and Xe by spin-polarized electrons in the near-threshold regime (Zeman *et al* 1997, 1998). It thus suggests a reasonable starting point for further detailed tests, particularly for angle-differential observables. Using this code for the present work, we have performed additional five-state

(RM5) and 15-state (RM15) calculations in order to assess the convergence of the close-coupling expansion with the number of states included, and thus to determine the need, or lack thereof, for a full RMPS calculation.

Two other existing computer codes based on perturbative approaches, namely the ‘unitarized first-order many-body theory’ (UFOMBT) and the ‘unitarized distorted-wave approximation’ (UDWA) by the Los Alamos group, are also available to us (Khakoo *et al* 1996). Note that UFOMBT calculations including an additional $5p^55d$ configuration (Fontes 1998) resulted in a much-improved agreement with experiment in Xe (Khakoo *et al* 1996) at low energies. Since for Xe the UDWA was shown not to perform as well as the UFOMBT, we do not include UDWA results in this paper.

For the present work we have performed UFOMBT calculations with a 12-configuration basis set to provide comparison between a first-order theory and the coupled-channel RM approach. Below we also show some predictions based upon the ‘relativistic distorted-wave approximation’ (RDWA) calculations of Zuo *et al* (1992) in which single-configuration target wavefunctions are used. Differential cross section (DCS) calculations for Kr have recently been carried out at $E_0 = 15$ eV by Stauffer (1998).

Scattering models are usually tested by comparing experimental and theoretical results for the *absolute* cross section or other *relative* observables such as spin and light polarizations. Angle-integrated and angle-differential examples for the latter in electron-impact excitation of noble gases include polarized-electron scattering asymmetries (Dümmler *et al* 1995), polarization of emitted radiation excited by spin-polarized electrons (Yu *et al* 1997a, b, Zeman *et al* 1997, 1998), or coherence and correlation parameters (Becker *et al* 1992). However, these experiments are difficult to undertake and hence the availability of such data is limited. On the other hand, differential cross section ratios (Khakoo *et al* 1994, 1996) provide alternative insights into the physics of scattering models for heavy rare gases. Such ratios can be measured very accurately and thus may provide an even more stringent test for theoretical models.

The present paper intends to demonstrate this latter approach for the case of Kr and to communicate the need for these ratios as important tests of theory. We therefore present new and accurate benchmark data of these ratios for electron-impact excitation of the $4p^55s$ configuration in Kr. This target was chosen because it exhibits significant spin-orbit interaction. The latter effect, however, is less important than in Xe and thus semi-relativistic theories might still be sufficiently accurate.

Following Khakoo *et al* (1994, 1996), we define an independent set of DCS (σ) ratios for our case of interest as follows:

$$r = \frac{\sigma(5s[3/2]_2)}{\sigma(5s'[1/2]_0)} \quad r' = \frac{\sigma(5s[3/2]_1)}{\sigma(5s'[1/2]_1)} \quad r'' = \frac{\sigma(5s[3/2]_2)}{\sigma(5s[3/2]_1)}. \quad (1)$$

To elucidate this choice, we express the $4p^55s$ levels in a simplified intermediate coupling scheme (Cowan 1981) with only the predominant configuration as

$$\begin{aligned} |5s[3/2]_2\rangle &= |5^3P_2\rangle \\ |5s[3/2]_1\rangle &= \alpha|5^3P_1\rangle - \beta|5^1P_1\rangle \\ |5s'[1/2]_0\rangle &= |5^3P_0\rangle \\ |5s'[1/2]_1\rangle &= \alpha|5^1P_1\rangle + \beta|5^3P_1\rangle. \end{aligned} \quad (2)$$

Values obtained for the intermediate-coupling mixing coefficients (α , β) were $(-0.673, 0.735)$ in the 12-configuration UFOMBT model and $(-0.739, 0.674)$ in the *R*-matrix model. The consequences of the apparent underestimation of the singlet-triplet mixing in the *R*-matrix models will be discussed further below.

From these equations, it follows that r relates to optically forbidden excitations to levels which, in this coupling scheme, are excited only via spin exchange. Note that $r \equiv 5$ in the

non-relativistic limit of degenerate fine-structure levels, i.e. it then corresponds to the *statistical branching ratio* for the $J = 2$ and 0 states. On the other hand, r' relates to optically allowed excitations. In the 'optical limit' of high incident electron energy E_0 and small scattering angle θ , the singlet portion of the $J = 1$ states is predominantly excited, and hence

$$\lim_{E_0 \rightarrow \infty} r' = \beta^2 / \alpha^2. \quad (3)$$

Deviations from these values may indicate (a) the importance of the triplet part of the $J = 1$ states, (b) the need to include additional configurations to describe these mixed levels or (c) the need to use a fully relativistic target description, including individual orbitals such as $4p_{1/2}$ and $4p_{3/2}$ instead of a non-relativistic $4p$ orbital. Finally, the r'' parameter completes the framework of these ratios by providing additional information on the optically forbidden excitations of the metastable levels *relative* to the resonant optically allowed transitions.

Note that one can achieve better accuracy in measurements of r , r' and r'' than in those of the individual DCSs, since only relative scattering intensities enter. Whilst careful measurements of inelastic DCSs may suffer from 15–25% uncertainty, measurements of ratios have typical uncertainties of 3–10%, since uncertainties introduced by normalization procedures to put the relative DCSs on an absolute scale do not enter. Ratio measurements therefore provide ideal parameters for rigorous tests of theoretical methods.

Our electron energy loss spectrometer utilizes double-hemispheric energy selectors both in the gun and analyser sections (Register *et al* 1980). It is housed in a clean vacuum environment with a base pressure of 1×10^{-7} torr. Inside the chamber, a demagnetized double mu-metal shield reduces the Earth's magnetic field to 1–2 mG. For present measurements, the spectrometer operated with an energy resolution of 30–40 meV (FWHM) with electron currents ranging from 3 to 20 nA. It was heated to about 120 °C to maintain the necessary stable conditions for taking electron energy loss spectra over long time periods. The kinetic energy of the incident electron beam was calibrated to within ± 0.05 eV by measuring the 2^2S resonance of He in the elastic channel at 19.366 eV. The angular calibration of the instrument was performed by determining the angular positions of well established minima in elastic scattering from Xe and Ne and is accurate to $\pm 1^\circ$. An advantageous feature of this spectrometer is the absence of 'wings' in the instrumental profile, often seen in spectrometers with single hemispherical analysers. This feature enabled us to separate weak energy loss features from nearby stronger ones. Spectra were measured several times during the course of these experiments to check the reproducibility as well as to improve statistics where required. We employed a well tested, sophisticated deconvolution program (Khakoo *et al* 1994, 1996) to determine separate spectral feature intensities. At our upper limit of resolution (≈ 30 meV), it was not necessary to unfold the spectra.

Measurements were made at incident electron energies of 12.0, 13.5, 15.0 and 20.0 eV, for θ ranging from 10° to 135° . The analyser detection efficiency for different energy loss electrons was determined by utilizing the existing time-of-flight data taken with Xe at $\theta = 90^\circ$ by the JPL group (LeClair and Trajmar 1996; see also Khakoo *et al* 1996) and the method described by Nickel *et al* (1989) using He. The detection efficiency as a function of energy loss was determined by comparing our inelastic to elastic ratios measured for groups of energy loss lines in the spectrum of Xe at $\theta = 90^\circ$ for the above energies. In all the calibration measurements, the gas beam was chopped to determine background contribution via a thin beam flag. These transmission calibrations were used to make adjustments to the values of the ratios r and r' in (1) to a precision of $\pm 5\%$. Thus, typical uncertainties in our experimental ratios r and r' include our transmission estimation (5%) plus statistical (0.5–10%) and fitting errors (0.5–25%), added in quadrature.

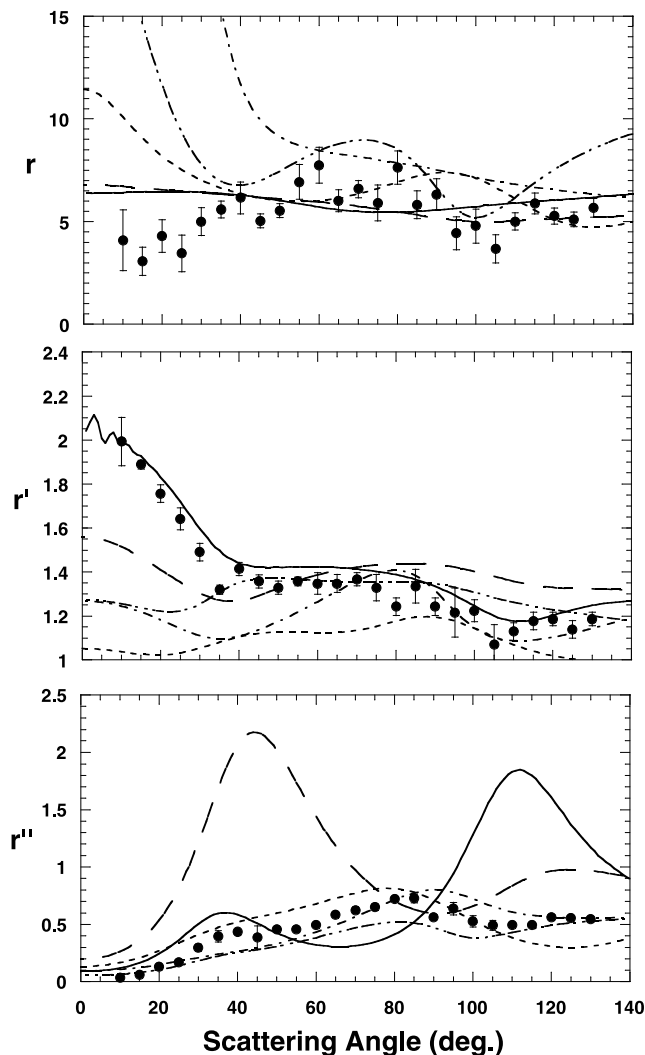


Figure 1. Ratios r , r' and r'' for Kr at $E_0 = 15.0$ eV. ●, present experiment with one standard deviation error bars. Present theories: —, UFOMBT; - - - -, RM5; - · - · -, RM15; - · - · -, RM31. Additional theory: - - - -, RDWA, Stauffer (1998).

Figure 1 shows the ratios introduced here at $E_0 = 15.0$ eV. We immediately observe remarkably good agreement for r' between experiment and the UFOMBT prediction over the entire range of θ . One might expect such good agreement for this quantity since it is the ratio of two allowed transitions, processes that are often well described by first-order theories. Agreement with the RDWA is not as good as with the UFOMBT, a result that could be due either to differences in the structure description or in the potentials used in the calculation of the distorted waves. The RM results disagree even more with experiment which may indicate a need for additional basis states in order to obtain convergence for this calculation.

Based upon equation (3), the optical limit of r' should be approximately 1.19 (UFOMBT) or 0.83 (RM) respectively, with a conservative uncertainty of not more than 5%. However, the experiment and the UFOMBT both give a much higher value of r' as $\theta \rightarrow 0^\circ$. The

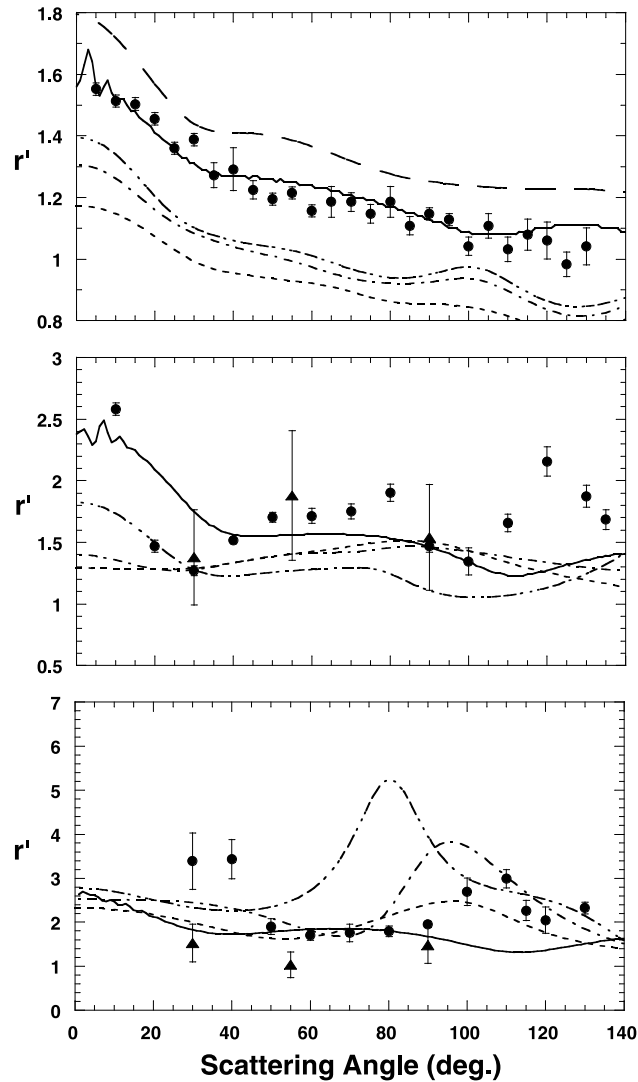


Figure 2. Ratios r' at $E_0 = 20.0$ eV (top), 13.5 eV (middle) and 12.0 eV (bottom). The legend is the same as for figure 1, except for \blacktriangle (Phillips 1982).

experimental value observed for small θ is approximately 2.1, i.e. a factor of 1.8 times larger than the optical limit value. To better understand this result, the UFOMBT was recalculated with the single-configuration scheme shown in equation (2), instead of the 12-configuration basis set. The value of r' obtained with this simplified scheme was nearly the same as the 12-configuration result over the entire angular range and $r'(\theta = 0^\circ) = 2.1$. Note that the RM models also predict a significantly larger value for r' than what would be expected from the corresponding structure results.

A possible mechanism for this large $r'(\theta = 0^\circ)$ value could be the projectile ion-core interaction. The weakness of coupling between the core and valence electron in Kr makes the angular momentum of the ion core more important than the entire configuration. The ratio of

the core statistical weights is 2:1 for the $[3/2]:[1/2]$ core j values in the $5s$ and $5s'$ levels. Angular momentum coupling with the core could explain these raised r' values being due to the core statistical weight ratio for the $5s[3/2]_1$ level as compared to the $5s'[1/2]_1$ level (Phillips 1982).

Our measurements of r (cf figure 1) confirm that this ratio dips significantly below the statistical weight value of 5 at around $\theta = 20^\circ$ and otherwise shows small undulations about the statistical weight value. As will be shown below, the rough quantitative agreement between experiment and the UFOMBT results is a coincidence in this case. Generally, the forbidden transitions that determine r are sensitive to second-order processes not addressed by the UFOMBT. Examining the UFOMBT results in finer detail shows a smooth r curve which dips at $\theta = 75^\circ$, in disagreement with the measured data, and also does not drop at small angles. Regarding the RM models, we see that the 31-state predictions for the r ratio rise significantly at small θ , as do the five- and 15-state RM r ratios. Also, the significant variation in the RM r ratios between the five-, 15- and 31-state calculations shows that the 31-state RM has not converged.

From an experimental point of view, r'' is the most accurate among the three ratio parameters. For this ratio, transmission corrections can be neglected, since the energy separation of the $5s[3/2]_2$ and the $5s[3/2]_1$ levels is only 0.118 meV and the residual energies of electrons from these scattering channels are nearly identical. In contrast to the situation for r' , the five-, 15-state and 31-state RM results in figure 1 show good agreement with experiment. In complete contrast, the UFOMBT does not give good agreement at all, a fact that we attribute to the inaccuracy of the calculated $J = 2$ cross section. There is also considerable disagreement for r'' with the RDWA, which predicts a large maximum at $\theta \approx 40^\circ$, in contrast to the experiment which shows a small bump. As far as agreement with experiment is concerned, the assessment regarding the reliability of the theoretical models is therefore exactly reversed for r' and r'' at this energy.

In figure 2, we show the trend of r' at different E_0 values. As can be seen, agreement with the UFOMBT is excellent at 20 eV, over the entire angular range. Agreement with the RDWA at 20 eV is qualitative, but the experimental data are about 20% lower than the theory. The RM gives a similar relative form for r' , but is quantitatively lower than experiment by about 15%. At lower incident energies, neither the UFOMBT nor the RM do very well. If the description of the target structure were sufficiently accurate, one would expect the RM to give better agreement with experiment at low E_0 values such as 12.0 and 13.5 eV, i.e. below

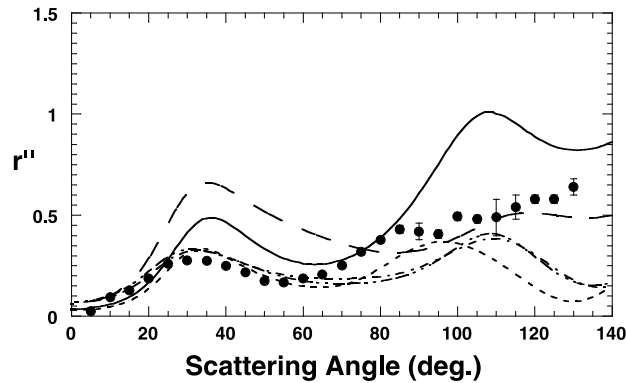


Figure 3. As in figure 1 for the ratio r'' at $E_0 = 20.0$ eV.

the ionization continuum—unless the results are affected by resonances. To investigate the presence of such resonance effects, the RM calculations were carried out around 12.0 eV in steps of 0.05 eV, but no rapid changes in the DCS ratios were observed. Once again we draw attention to the large values of r' for $\theta = 0^\circ$ observed at these energies, similarly to the case at $E_0 = 15.0$ eV. At 13.5 and 12.0 eV, we also include the data of Phillips (1982) which are the only other results available at these energies. These data are accurate to $\pm 20\%$ and were measured only at the three scattering angles of $\theta = 30^\circ, 55^\circ$ and 90° . Within the error bars, they are in excellent agreement with our experimental results.

In figure 3, we show our r'' values at $E_0 = 20.0$ eV. At scattering angles below 60° , the

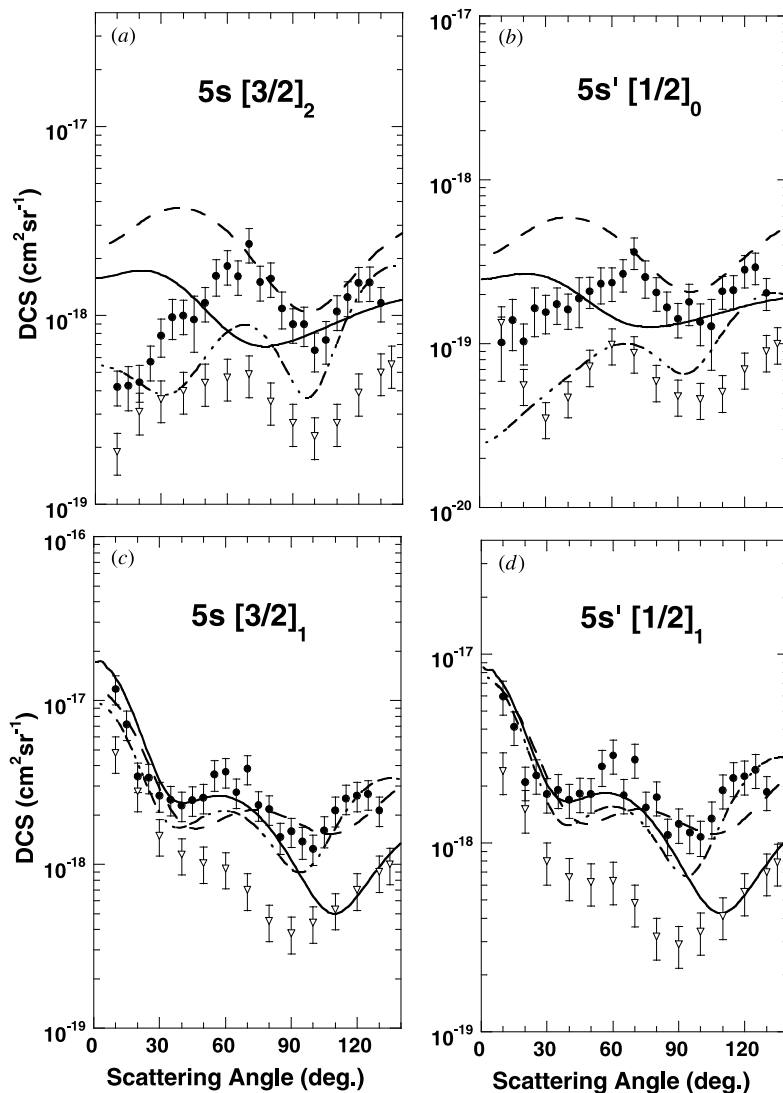


Figure 4. DCS results for electron-impact excitation of the (a) $5s[3/2]_2$, (b) $5s'[1/2]_0$, (c) $5s[3/2]_1$ and (d) $5s'[1/2]_1$ levels of Kr at $E_0 = 15.0$ eV. The legend is as in figure 1, except for: ∇ , Srivastava *et al* (1981). For the RM results only RM31 is displayed.

RM5, RM15 and RM31 calculations converge together and are in excellent agreement with experiment to within 10% over this range. However, at $\theta > 60^\circ$, the predictions from the three models diverge from each other and from the experimental values. Neither RDWA nor UFOMBT agree with experiment for r'' even at this relatively high incident energy.

To further investigate the possible reasons for agreement or disagreement between the theoretical predictions and the measured data, we show in figure 4 recently measured absolute DCSs at 15 eV for the transitions currently under consideration. They were obtained by normalization of scattering intensities in the electron energy loss spectra to the elastic DCSs of Danjo *et al* (1988). The major contribution to the uncertainty in our DCSs is that in the elastic DCS. Figure 4 clearly reveals the reason for the major discrepancies between the RM predictions and experiment for r at small angles. Although the angular dependence of the $J = 0$ and 2 DCSs predicted by the RM model is in qualitative agreement with experiment, the results for the $5s'[3/2]_2$ state (figure 4(a)) are overestimated at small angles. This situation offers a good example of how r may indeed provide a more sensitive test of the theoretical DCSs than the individual DCSs.

Although r was predicted quite well by the UFOMBT at 15 eV, figures 4(a) and (b) reveal that this result is accidental, since both the shape and the magnitude of the DCSs for the individual transitions are not predicted well at all. As mentioned above, this is not unexpected of such a perturbative approach. However, the UFOMBT does much better for the dipole-allowed transitions, as seen in figures 4(c) and (d). Whereas both theories yield excellent small-angle shapes for these transitions, the UFOMBT predicts a better value for the DCS ratio r' while the RM gives a better overall shape. Clearly, both models need significant improvement with regard to the detailed quantitative description of the collision process.

In conclusion, we have shown how DCS ratios for electron-impact excitation of the $4p^55s$ configuration of Kr can be used as a sensitive probe of target relativistic effects. Comparison of theory and experiment for these parameters and the absolute DCS provides useful information regarding where present theoretical models for electron collisions with the heavy rare gases can be improved.

This work was supported by the National Science Foundation under grant numbers NSF-RUI-PHY-9511549 (MAK) and NSF-PHY-9605124 (VZ and KB) and by NATO under grant number CRG-950003 (AC and MAK). We thank Professor T J Gay for helpful discussions, D Parsons, H Fabris and J Buell for technical support, D Roundy for writing the spectrum fitting code for this work and Professor A D Stauffer for providing the RDWA results.

References

- Bartschat K 1998a *J. Phys. B: At. Mol. Opt. Phys.* **31** L469
 ———1998b *Comput. Phys. Commun.* **114** 168
 Bartschat K, Burke P G and Scott M P 1997 *J. Phys. B: At. Mol. Opt. Phys.* **30** 5915
 Bartschat K, Hudson E T, Scott M P, Burke P G and Burke V M 1996 *J. Phys. B: At. Mol. Opt. Phys.* **29** 115
 Becker K, Crowe A and McConkey J W 1992 *J. Phys. B: At. Mol. Opt. Phys.* **25** 3885
 Berrington K A, Eissner W and Norrington P H 1995 *Comput. Phys. Commun.* **92** 290
 Bray I 1994 *Phys. Rev. A* **49** 1066
 Bray I and Stelbovics A T 1992 *Phys. Rev. A* **46** 6995
 Cowan R D 1981 *The Theory of Atomic Structure and Spectra* (Berkeley, CA: University of California Press)
 Danjo A 1988 *J. Phys. B: At. Mol. Opt. Phys.* **21** 3759
 Dümmler M, Hanne G F and J Kessler J 1995 *J. Phys. B: At. Mol. Opt. Phys.* **28** 2985
 Fontes C J 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** 175
 Fursa D V and Bray I 1997 *J. Phys. B: At. Mol. Opt. Phys.* **30** 757
 Hudson E T, Bartschat K, Scott M P, Burke P G and Burke V M 1996 *J. Phys. B: At. Mol. Opt. Phys.* **29** 5513

- Khakoo M A, Beckmann C E, Trajmar S and Csanak G 1994 *J. Phys. B: At. Mol. Opt. Phys.* **27** 3159
- Khakoo M A, Trajmar S, LeClair L R, Kanik I, Csanak G and Fontes C J 1996 *J. Phys. B: At. Mol. Opt. Phys.* **29** 3455
- LeClair L R and Trajmar S 1996 *J. Phys. B: At. Mol. Opt. Phys.* **29** 5543
- Nickel J C, Zetner P W, Shen G and Trajmar S 1989 *J. Phys. E: Sci. Instrum.* **22** 730
- Phillips J M 1982 *J. Phys. B: At. Mol. Phys.* **15** 4259
- Register D F, Trajmar S and Srivastava S K 1980 *Phys. Rev. A* **29** 1134
- Srivastava S K, Tanaka H, Chutjian A and Trajmar S 1981 *Phys. Rev. A* **23** 2156
- Stauffer A D 1998 Private communication
- Trajmar S, Kanik I, Khakoo M A, LeClair L, Bray I, Fursa D V and Csanak G 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** L393
- Yu D H, Hayes P A, Furst J E and Williams J F 1997a *Phys. Rev. Lett.* **78** 2724
- Yu D H, Hayes P A, Williams J F and Furst J E 1997b *J. Phys. B: At. Mol. Opt. Phys.* **30** 1799
- Zeman V, Bartschat K, Gay T J and Trantham K W 1997 *Phys. Rev. Lett.* **79** 1825
- Zeman V, Bartschat K, Norén C and McConkey J W 1998 *Phys. Rev. A* **58** 1275
- Zuo T, McEachran R P and Stauffer A D 1992 *J. Phys. B: At. Mol. Opt. Phys.* **25** 3393