RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 30, NUMBER 6 DECEMBER 1984

Electron spectroscopy of multiple ionization of argon by electron impact

R. Hippler,* K. Saeed, A. J. Duncan, and H. Kleinpoppen
Atomic Physics Laboratory, University of Stirling, Stirling FK9 4LA, United Kingdom
(Received 20 July 1984)

Doubly differential cross sections (DDCS) for electron ejection in electron-argon collisions have been studied for ejected electron energies 25 to 300 eV, ejection angle $\theta_\delta = 90°$, and incident electron energies of 300 eV to 8 keV. Performing a charge-state analysis of the recoil ion in coincidence with the ejected electron, we were able to distinguish between singly and multiply ionizing collisions. It was observed that the relative importance of multiple ionization events increases with increasing energy of the ejected electron. At an ejected electron energy corresponding to *LMM* Auger transitions, Ar^{2+} and Ar^{3+} are predominantly produced by *L*-shell ionization. From an analysis of the corresponding DDCS, information about simultaneous *L*- and *M*-shell ionization is obtained.

I. INTRODUCTION

Recently, there has been an increasing interest in the study of multiple ionization events. While a large body of data already exists for photoionization,[1,2] studies of ionization by particle impact seem to be only at their beginning (e.g., Refs. 3–6, and references therein). Experimental investigations by particle impact have so far made use of the detection of multiply charged ions (e.g., Ref. 7, and references therein), or used vacuum ultraviolet,[8] Auger electron,[9,10] or x-ray spectroscopy.[11] Few attempts have been made to measure energy and angular differential cross sections for electron ejection in multiple ionizing collisions. Van der Wiel and Wiebes[12] have obtained energy differential cross sections for multiple ionization in electron-argon collisions measuring the energy loss of the incident electron in coincidence with the ions of a certain charge state. The present investigation is similar to the recent work of Hippler, Bossler, and Lutz,[6] who measured doubly differential cross sections for electron ejection in proton–rare-gas collisions in coincidence with the product ion, thereby obtaining the different contributions from singly and multiply ionizing collisions. In particular, we have investigated the following process

$$e^- + \mathrm{Ar} \rightarrow [ne^-] + \mathrm{Ar}^{n+} + e_\delta^- \quad . \tag{1}$$

Detection of the product ion in coincidence with the ejected electron (e_δ^-) allows identification of *n*-fold ionization events. No information is obtained on the systems within the square brackets, which would require a higher-order coincidence experiment.

II. EXPERIMENTAL PROCEDURE

The experimental arrangement has been described in some detail previously.[13] The measurements have been performed by injecting an energetic electron beam into a dilute argon gas target. Ions produced by the ionization process were extracted from the collision region by a small electric field (about 25 V/cm) between a lower plate and an upper grid, both of 1 cm diameter and separated 1 cm from each other. The target gas was introduced into the chamber through a small orifice in the lower plate. Electrons ejected at 90° with respect to the incident electron direction and perpendicular to the direction of the electric field for ion detection were detected in a 30°-parallel plate electrostatic analyzer. In order to increase its detection efficiency, the analyzer was operated with a modest energy resolution of about 12% full width at half maximum (FWHM). No significant change in the measured energy distribution of the ejected electrons with and without applied electric field was observed, provided the electron kinetic energy was corrected to allow for the potential difference between target and electron analyzer.

Electrons ejected in an *n*-fold ionization process were identified by simultaneous detection of the product ion. The ionic charge state was determined in a time-of-flight (TOF) setup, measuring with the help of standard coincidence electronics (time-to-pulse height converter, multichannel analyzer) the time delay of the product ion relative to the ejected electron. Typically, this time delay was of the order of few μs; depending on the ionic charge state and mass and the length of the TOF drift tube (about 3 cm). Several peaks corresponding to ionic charge states $n=1$ up to $n=4$ were observed in the time spectra. After subtracting random coincidences, the number of true coincidences, $N_c^{(n)}$ were related to a doubly differential cross section (DDCS) for *n*-fold ionization, $d^2\sigma^{(n)}/(dE\,d\Omega)$, by

$$d^2\sigma^{(n)}/(dE\,d\Omega) = (N_c^{(n)}/N_i)\sigma_i/(\Delta E \Delta\Omega \epsilon_\delta) \quad . \tag{2}$$

σ_i is the total cross section for ion production, N_i the number of detected ions, ϵ_δ the efficiency of the electron detection system, and ΔE and $\Delta\Omega$ energy bandwidth and solid angle of the electron analzyer, respectively. For the total ionization cross section σ_i we used the cross sections for $3s$ and $3p$ ionization given by McGuire,[14] extrapolated to higher incident electron energies with the help of Bethe's formula (see, e.g., Ref. 15)

$$\sigma_i = (I/E)[A\ln(E/I) + B] \quad . \tag{3}$$

Here, E is the incident electron energy, I the ionization energy for a particular subshell, and A and B are two constants determined from McGuire's calculations. The inner shell (K, L shell) contribution to the total ionization cross section is negligibly small; its largest contribution is at 8 keV where it accounts for less than 4% of σ_i. Alternatively, one could have used experimental cross sections[3] for σ_i, which on an absolute scale deviate about 15% from McGuire's data and show a slightly different energy dependence. ϵ_δ and $\Delta\Omega$ have been assumed to be independent of the electron energy in the range of interest here (25–300 eV). No attempt was made, however, to determine ϵ_δ and $\Delta\Omega$ absolutely. Therefore, only relative DDCS were obtained.

III. RESULTS AND DISCUSSION

Spectra for ejected electrons coincident with argon ions of different charge states are given in Fig. 1 for 0.7-keV incident electron energy. The kinetic energy E_δ of the detected electron was varied between about 30 and 260 eV. Ionic charge states up to $n=4$ were detected. At low electron energies singly charged ions are the most abundant. This changes in the vicinity of the Ar-L Auger transitions around 200 eV. There, Ar^{2+} and Ar^{3+} are more abundant than Ar^{+} by a factor of about 8 and 4, respectively. At 260 eV Ar^{+}, Ar^{2+}, and Ar^{3+} have about the same abundance. A singly differential (with respect to the kinetic energy E_δ of the ejected electron) electron spectrum calculated in the plane-wave Born approximation (PWBA)[16] using analytical M-shell form factors given by Choi,[17] agrees satisfactorily with the continuous part (i.e., excluding the L-shell Auger part around 200 eV) of the electron spectrum obtained by summing the spectra for the four different ionic charge states. One may conclude from this comparison that, as far as the ejected electron energy dependence is concerned, the experimental sum spectrum is in reasonable agreement with predictions from standard theoretical descriptions.[18]

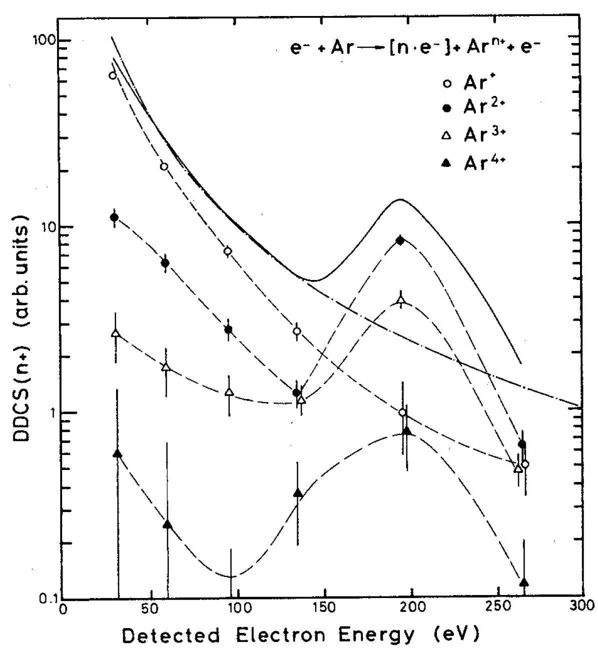

FIG. 1. Doubly differential cross sections (DDCS) for n-fold ionization vs energy of the detected electron for 0.7-keV electrons incident on argon. The ejection angle is 90°. Data are obtained in coincidence with ○ Ar^{+}, ● Ar^{2+}, Δ Ar^{3+}, and ▲ Ar^{4+} ions. The solid line gives a sum spectrum obtained by summing the four DDCS(n+) spectra. The dashed-dotted curve is a singly differential cross section ($d\sigma/dE$) for electron ejection calculated in PWBA with analytical M-shell form factors (see text). Dashed lines are to guide the eye only.

Of special interest are the characteristic (Auger) parts of the electron spectra around 200 eV. At this ejected-electron energy the ionic charge states 2+ and 3+ are chiefly produced by L-shell ionization, whereas singly charged ions result from M-shell ionization or from L-shell excitation processes, resulting, for instance, in $2p^5\ nl$ final states. Therefore, an analysis of the DDCS ($n+$) at this particular ejected-electron energy may provide information about $L1$ and $L23$ ionization. Assuming that Auger electrons are ejected isotropically, which is a reasonable assumption since the corresponding alignment is small (see, e.g., Refs. 15 and 19), and neglecting contributions from multiple M-shell ionization [i.e., from the (continuous) electron background under the Auger peaks], the DDCS(2+) and DDCS(3+) at $E_\delta = 200$ eV are proportional to the total cross sections $\sigma(L1)$ and $\sigma(L23)$ for $L1$- and $L23$-shell ionization, respectively. According to Van der Wiel and Wiebes[12]

$$\begin{aligned} &\mathrm{DDCS}(2+) \propto 0.89\sigma(L23)\ , \\ &\mathrm{DDCS}(3+) \propto 0.84\sigma(L1) + 0.92\sigma(L23)S\ , \end{aligned} \tag{4}$$

where S is the so-called shake-off probability following L-shell ionization. Here, we have omitted double L-MMM Auger processes[20] which result in ejection of two electrons but do not contribute to the DDCS at $E_\delta = 200$ eV.

In Fig. 2 doubly differential cross sections are given for electron ejection in 0.3- to 8-keV electron-argon collisions. These cross sections have been measured for an ejected electron energy of 200 eV, an ejection angle $\theta_\delta = 90°$, and in coincidence with ions of charge states 1+ to 3+. As has been noted above, at this ejected-electron energy the ionic charge states 2+ and 3+ are chiefly produced by L-shell ionization. The experimental DDCS(2+) and DDCS(3+) may be compared with calculations of McGuire[14] for $L23$ and $L1$ ionization. The two curves in Fig. 2 have been

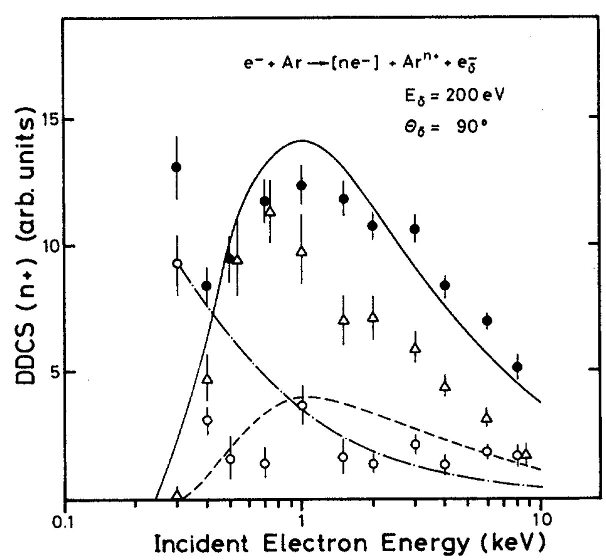

FIG. 2. Doubly differential cross sections DDCS for production of n-fold charged argon ions at an ejected electron energy of 200 eV vs incident electron energy. The ejection angle is 90°. Present measurements are for ○ Ar^{+}, ● Ar^{2+}, and Δ Ar^{3+}. Solid and dashed lines given the L-shell contribution with $S=0$ [Eqs. (4)] to DDCS(2+) and DDCS(3+), respectively. The dashed-dotted line is a singly differential cross section for M-shell ionization (see text).

derived according to Eqs. (4) with $S=0$. Good agreement with the experimental DDCS(2+) data is obtained, except at small incident energies. There, the discrepancy is probably due to double M-shell ionization events. In contrast to this, the DDCS(3+) data differ by about a factor of 2 from the predictions of the calculation. Most probably, this is caused by the neglect of simultaneous L- and M-shell ionization. Such multiple ionization events may be the result of different mechanisms. For instance, if ionization is treated as some statistical process, there is a certain probability for producing two (or more) instead of only one electron. If P_L and P_M are the ionization probabilities for L- and M-shell ionization, respectively, the probability for LM^n ionization is proportional to $P_L P_M^n$. Thus, if P_M decreases, for instance with increasing incident electron energy, the relative fraction of multiple LM^n ionization events compared to single L-shell ionization will decrease as P_M^n and become negligible for sufficiently small P_M. This ionization probability depends on the energy of the incident electron. There is an additional contribution which is independent of the incident energy. This contribution results from a rearrangement of the electron cloud after removal of a single electron (shake-off). It is accounted for in Eqs. (4) by putting $S>0$. A reasonable number for the shake-off probability following L-shell ionization is $S=0.16$.[12]

In Fig. 3 we have plotted the cross section ratio DDCS(3+)/DDCS(2+) for the experimental conditions discussed above ($E_\delta=200$ eV, $\theta_\delta=90°$) versus incident electron energy. Also given in this comparison is an experimental data point obtained at an incident electron energy of 10 keV by Van der Wiel and Wiebes,[12] which connects reasonably well to our data. The experimental data are compared with two theoretical curves, derived from Eqs. (4) with $S=0$ and $S=0.16$, respectively. Obviously, the experimental data are inconsistent with these theoretical predictions. The deviations at large incident electron energies may have at least two causes. One cause might be that the shake-off probability used in the comparison ($S=0.16$) has been chosen too large. The other reason might be of instrumental origin. Since the detection of efficiencies for ions with different charge states (and different kinetic energies) were not known a charge-state independent efficiency was assumed. In addition, the measurements were performed with a fixed kinetic energy of about 200 eV for the detected electron. It is known that Auger transitions in multiply charged ions may be shifted to lower transition energies (about 20 eV per charge state increase, see, e.g., Ref. 6). Both effects are likely to introduce some experimental uncertainty in the absolute value of the cross-section ratio. Even then, the energy dependence of the experimental DDCS(3+)/DDCS(2+) ratio is remarkably different from the theoretical prediction. This shows that the experimental data are not in agreement with a constant probability for simultaneous L- and M-shell ionization. A similar observation was made by Carlson, Moddeman, and Krause[9] for simultaneous LM ionization of argon by incident electrons with kinetic energy up to 3 keV, and recently also by Löw, Genz, Richter, and Dyall,[21] who found that the total cross section for simultaneous K- and L-shell ionization relative to the cross section for K-shell ionization was energy dependent. The relative magnitudes of the energy-dependent contribution to the simultaneous LM-ionization processes in the present and measurements of Carlson *et al.*[9] are different, however. Furthermore, the latter measurements indicate that energy-independent simultaneous LM ionization dominates for incident energies about 2 keV, which is not obvious from the present data. This indicates that these two experiments, being of different type, probe somewhat different aspects of multiple ionization processes. A theoretical investigation of the two contributions to multiple ionization events has been made recently by McGuire[22] for proton and electron impact on helium. For impact ionization of argon no such detailed analysis yet exists.

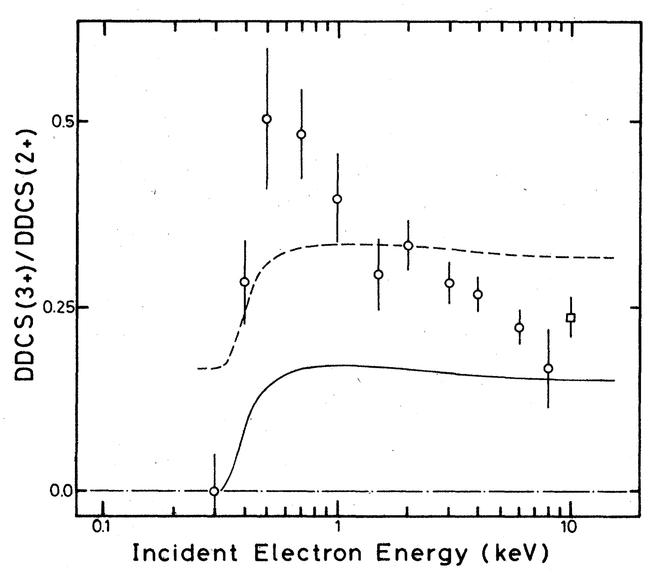

FIG. 3. Cross-section ratio DDCS(3+)/DDCS(2+) for production of triply and doubly charged argon ions at an ejected electron energy of 200 eV vs incident electron energy. The ejection angle is 90°. The present measurements (○) and those of Van der Wiel and Wiebes (Ref. 12) (□) are compared with the predictions of Eqs. (4) with $S=0$ (solid line) and $S=0.16$ (dashed line) using total cross sections for L-shell ionization calculated in PWBA (see text).

Also given in Fig. 2 are experimental results for DDCS(1+). They are compared with a singly differential cross section $d\sigma/dE$ calculated in PWBA using M-shell form factors of Choi.[17] The experimental DDCS(1+) decreases by almost one order of magnitude when the incident electron energy is increased from 300 to 500 eV; it remains approximately constant (with the exception of the 1-keV data point) from 500 eV up to 8 keV. In contrast, the theoretical $d\sigma/dE$ decreases monotonically over the entire energy range. We do not think that the large difference between the theoretical $d\sigma/dE$ and the experimental DDCS(1+) can be accounted for by an energy-dependent anisotropy of the electron-ejection process. Therefore, it might be concluded from the strong decrease of DDCS(1+) after the onset of L-shell ionization that there is some correlation or competition between M- and L-shell ionization at this particular ejected electron energy.

ACKNOWLEDGMENTS

We would like to thank Professor H. O. Lutz for helpful discussion. Part of this work was supported by the British Science and Engineering Research Council (SERC) and by a travel grant (R.H.) from the Deutsche Forschungsgemeinschaft (DFG). One of us (K.S.) acknowleges receipt of a scholarship from the University of Mosul (Iraq).

*Permanent address: Fakultät für Physik, Universität Bielefeld, Bielefeld, Federal Republic of Germany.

[1]J. A. R. Samson, in *Corpuscles and Radiation in Matter I,* edited by W. Mehlhorn, Handbuch der Physik, Vol. XXXI (Springer-Verlag, Berlin, Heidelberg, 1982), p. 123.

[2]A. F. Starace, in Ref. 1, p. 1.

[3]P. Nagy, A. Skutlartz, and V. Schmidt, J. Phys. B **13**, 1249 (1980).

[4]C. Achenbach, A. Müller, E. Salzborn, R. Becker, J. Peschina, and H. Klein, in *Proceedings of the Thirteenth International Conference on the Physics of Electronic and Atomic Collisions, Berlin, 1983, Abstracts of Contributed Papers,* edited by J. Eichler, W. Fritsch, I. V. Hertel, N. Stolterfoht, and U. Wille (ICPEAC, Berlin, 1983), p. 200.

[5]T. Hirayama, K. Oda, T. Ono, Y. Morikawa, K. Wakiya, and H. Suzuki, in Ref. 4, p. 201.

[6]R. Hippler, J. Bossler, and H. O. Lutz, J. Phys. B **17**, 2453 (1984).

[7]S. T. Manson, R. D. DuBois, and L. H. Toburen, Phys. Rev. Lett. **51**, 1542 (1983).

[8]H. F. Beyer, R. Hippler, K.-H. Schartner, and R. Albat, Z. Phys. A **289**, 239 (1979); **292**, 353 (1979).

[9]T. A. Carlson, W. E. Moddeman, and M. O. Krause, Phys. Rev. A **1**, 1406 (1970).

[10]N. Stolterfoht, F. J. de Heer, and J. van Eck, Phys. Rev. Lett. **30**, 1159 (1973).

[11]H. Oona, Phys. Rev. Lett. **32**, 571 (1974).

[12]M. J. Van der Wiel and G. Wiebes, Physica **53**, 225 (1971).

[13]R. Hippler, K. Saeed, I. McGregor, and H. Kleinpoppen, Z. Phys. A **307**, 83 (1982); R. Hippler, H. Klar, K. Saeed, I. McGregor, A. J. Duncan, and H. Kleinpoppen, J. Phys. B **16**, L617 (1983).

[14]E. J. McGuire, Phys. Rev. A **16**, 62 (1977).

[15]R. Hippler, in *Progress in Atomic Spectroscopy, Part C,* edited by H. J. Beyer and H. Kleinpoppen (Plenum, New York, 1984), p. 511.

[16]R. Hippler and W. Jitschin, Z. Phys. A **307**, 287 (1982).

[17]B.-H. Choi, Phys. Rev. A **7**, 2056 (1973).

[18]It should be kept in mind that due to the anisotropy of the electron ejection a comparison between a singly and doubly differential cross section requires some caution.

[19]W. Mehlhorn, in *Proceedings of the International Seminar High-Energy Ion-Atom Collision Processes, Debrecen (1981)* (Akademiai Kiado, Budapest, 1983), p. 83.

[20]T. A. Carlson and M. O. Krause, Phys. Rev. Lett. **17**, 1079 (1966).

[21]W. Löw, H. Genz, A. Richter, and K. G. Dyall, Phys. Lett. **100A**, 130 (1984).

[22]J. H. McGuire, Phys. Rev. Lett. **49**, 1153 (1982).