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Electron impact ionisation cross section of krypton (σ_{n+}, $n = 2$–7)

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Abstract

Multiple ionisation cross section of krypton (Kr–Kr^{n+}, with $n = 2,7$) have been measured by time-of-flight spectrometry in the 100–3000 eV electron impact energy range. We determined the apparent ionisation thresholds and the integrated oscillator strengths for the reactions. The values are compared with data available in the literature. (Int J Mass Spectrom 184 (1999) 49–56) © 1999 Elsevier Science B.V.

Keywords: Multiple ionisation; Cross sections; Krypton

1. Introduction

Multiple ionisation cross sections (MICS) of atoms by electronic collision are needed in many fundamental applications in different technological and scientific areas. There is increasing interest in these reactions for atoms, which is partly because of the additional physical processes that involve electronic correlation effects. Nevertheless, only few multiple ionisation measurements for krypton are available in the literature. Frequently, only a particular experimental technique has been adopted. Some authors [1–5] have revealed discrepancies in both magnitude and energy dependence of cross sections reported by different groups. Tarnovsky and Becker [1] and Bruce and Bonham [2] discussed the possible sources for the differences in the absolute values of cross sections for ionisation of noble gases reported by laboratories using various techniques. Experimental improvements, such as new generation detectors and time-resolved techniques, made possible more accurate cross section measurements. Some of the disagreements have also been attributed to autoionisation states present in the target final state [4,5].

An extensive review on the most common theories can be found in Märk and Dunn [6] and reference cited therein. In the last decade several efforts have been made to derive calculation schemes for multiple ionisation cross sections [7–10]. Treatments based upon *ab initio* quantum mechanics are difficult because they involve several charged particles interacting with a long-range coulomb potential. Hence, empirical and classical methods have been developed in order to obtain reasonably accurate cross sections for multiple ionisation by electron impact. Theoretical

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groups [7–10] have derived empirical expressions that were found to agree well with a variety of experimental ionisation cross sections.

There are mainly two processes that can lead to a particular degree of multiple ionisation of the target atom. First, in the sudden limit the electron is regarded as being removed from one particular inner shell. The target atom, now ionised, is left in an excited state giving rise to a subsequent electron emission cascade. Second, the direct outer-shell ionisation with simultaneous electron ejection may occur in the slow velocity regime. The outgoing electrons experiment the continuous adjustment of the potential from the residual target. The processes, in which multiple ionisation reaction occurs, have been investigated using photoionisation data [11,12]. Tunable monochromatic synchrotron radiation with energy of hundreds of electron volts has now become available with energy spreads lower than the natural linewidths of the inner-shell states of about 10^{-1} eV. Using these photon beams, photoabsorption measurements can be made to determine spectroscopic energies and multiple ionization yields [13]. In this way the decay modes of the inner-shell states can be elucidated. Electron impact, however, is also a powerful way of studying inner-shell states of atoms. It has provided much information about the ionization of these states and their spectroscopic parameters. A particular advantage of electron impact is its ability to excite inner-shell states that are optically forbidden from the ground state. Electron impact at high energy and small scattering angle, where the Born approximation is valid, may be quantitatively related to the optical oscillator strength. In this picture, the incident electron simulates a virtual photon field and dipolar transitions are dominant. In contrast, dipole selection rules cannot be applied at low impact energies, particularly at large scattering angles, and thus optically forbidden processes may be observed. Hence, theoretical approaches based on the Bethe-Born approximation cannot properly describe those reactions. The matrix-element squared M_n^2 is obtained by integrating the dipole oscillator strength for the processes considered. Models for describing the integrated oscillator strength (IOS) have become an important tool in understanding electron–atom ionisation collisions [11,12].

The aim of the present article is to obtain experimentally the cross sections, the integrated oscillator strength, and the apparent threshold energies for the multiple ionisation of krypton by electrons of 100–3000 eV incident energies. We also attempt to identify those processes where the Born approximations can give a reasonable description.

2. Experimental apparatus

A detailed description of the experimental setup has been given elsewhere [14]. Briefly, the experiment was done in a time-of-flight (TOF) mass-to-charge spectrometer. Pulses of electrons (of 100 ns duration) are accelerated toward a static gas cell by a triode electron gun based on a directly heated tungsten hairpin filament. The diameter of the electron beam was not measured directly, but the beam profile was analysed with the aid of the SIMION [15] program. This system provides a well defined beam at the target with an adjustable energy of 100–3000 eV and an energy spread of ~2 eV, which has been determined by the retarding potential method [16].

The interaction region of 3 cm long is filled with research grade gas to pressures up to around 0.1 mTorr, to ensure single-collision conditions. The experimental apparatus is housed in a 24 L stainless-steel cylindrical chamber pumped by a 6 in. diffusion pump with a liquid-N_2 cryotrap and the base pressure was always maintained lower than 10^{-6} Torr during the operation run. The static gas target (pumped by a differential technique) offers an important advantage for the present study. This is useful because the high density of scattering atoms compensates for the low multiple ionisation cross sections (10^{-18}–10^{-20} cm^2). Immediately following each electron pulse, a 24 V/cm electric field is applied briefly across the interaction region. Therefore, the ionisation takes place in a free field region. After the ions pass through the drift tube (Willey-McLaren type [17]) they are detected by to a set of microchannel plates assembled in a chevron arrangement.

Special attention has been paid to the incomplete collection and detection of the ions [2]. The most serious problem is the ion loss during their flight to the detector, which is due to the electron capture by the ion in collisions with the background gas. The electronic capture cross section at 50 V accelerating potential, estimated by the Landau-Zener model [18], is lower than 3×10^{-17} cm^2. Therefore, only around 0.1% of the ions are removed from their initial charge state and the effect of incomplete ion collection is well covered within the total uncertainty.

We have considered the experimental arguments of Bruce and Bonham [2] for all measurements carried out. For example, the accelerating potential at the entrance of the microchannel plate was 5 kV and the constant fraction discriminator was adjusted to about 50 mV. In our case, the measured ratios σ_{2+}/σ_{+} for argon agree within the uncertainty with well established previously reported data [19–23] for 100 and 500 eV electron impact energies. The same ratio analysis has been performed for neon [5] showing good agreement with the data in the literature.

3. Results and discussion

Fig. 1 shows a typical time-of-flight spectrum of the species detected for a 1000 eV electron impact. Our resolution is not good enough to resolve the various krypton stable isotopes, therefore all cross sections throughout this article have been obtained by integrating over all isotopes. The reaction are represented by

$$e^- + \mathrm{Kr} \rightarrow \mathrm{Kr}^{n+} + (n+1)e^- \qquad (1)$$

where n is the number of electrons extracted from the krypton atom.

Obtaining the absolute ionisation cross section of atomic and molecular species presents a serious experimental challenge as far as normalisation is concerned. Determination of the effective target thickness is still the major problem, especially if the windowless static gas target technique is adopted. All cross sections were determined from the ratio of the ion abundance. The results are free from uncertainties due to absolute pressure measurements and fitting procedures. Subsequently, our data have been normalised to the values of Rapp and Englander-Golden [24]. We considered the total ionisation cross section as $\sigma_{\mathrm{tot}} = \Sigma_n n\sigma_{n+}$ and $I^{\mathrm{tot}} = \Sigma_n nI^{n+}$, where I^{n+} is the Kr^{n+} yield at each impact energy.

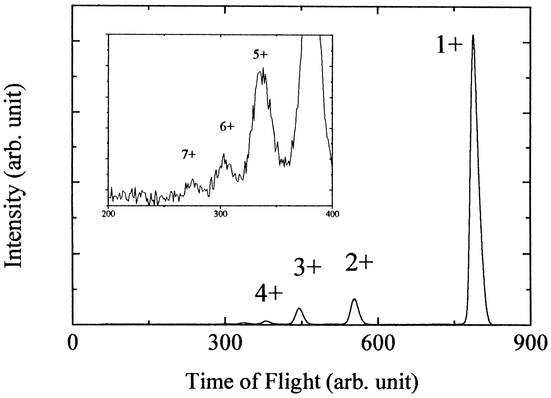

Fig. 1. Time-of-flight spectrum of Kr^{n+}ionised by 900 eV impact electrons.

The total uncertainties of the normalised ionisation cross section (NICS) result from the standard statistical errors added in quadrature (independent measurements) for the quantities used in the normalisation

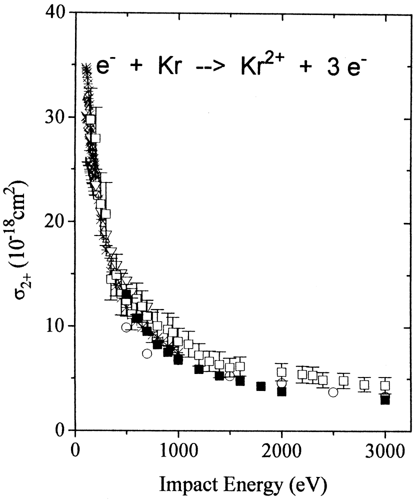

Fig. 2. Electron impact ionisation cross section σ_{2+} as a function of the incident energy. □ present data; ○ Nagy et al. [20]; + Stephan et al. [21]; × Wetzel et al. [22]; * Krisnakumar and Srivastava [26]; △ Syage [27]; ▽ Lebius et al. [28]; ■ Schram [25].

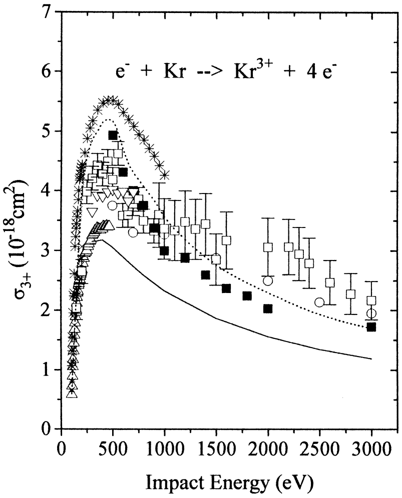

Fig. 3. Electron impact ionisation cross section σ_{3+} as a function of the incident energy. □ present data; ○ Nagy et al. [20]; + Stephan et al. [21]; × Wetzel et al. [22]; * Krisnakumar and Srivastava [26]; △ Syage [27]; ■ Schram [25]; ··· Fisher et al. [7]; — Shevelko and Tawara [8].

procedure. The statistical counting uncertainties for I^{n+}/I^{tot} $(n = 2\text{–}7)$, after subtracting the background, were approximately 0.1%, 0.3%, 1%, 3%, 12%, and 14%, respectively. Considering that the data from [24] are reliable within 7% (as quoted by the authors), the overall uncertainties of the present NICS are about 7%, 7%, 7.2%, 8%, 13%, and 18% for σ_{2+}–σ_{7+}, respectively. The total uncertainty is shown for each experimental data point in Figs. 2–7. The incident energy spread less 2 eV could be relevant in the threshold region.

3.1. Multiple ionisation cross sections

Normalised ionisation cross section σ_{n+} for electron collision on Kr are compared in Figs. 2–7 to the previous experimental results [20–22,25–28] and theoretical methods [7–9] available in the literature ranging from threshold to 3000 eV. Shevelko and Tawara (ST) [8] have presented a semiempirical formula for multiple ionisation cross sections for atoms and ions by electron impact deduced on the basis of the Bethe-Born dependence of σ_n on the incident energy. Their simple formula depends only on three atomic parameters (the minimal ionisation potential, the atomic number of the target atom, and the degree of ionisation). Deutsch et al. [9] have recently extended the DM formalism, which was

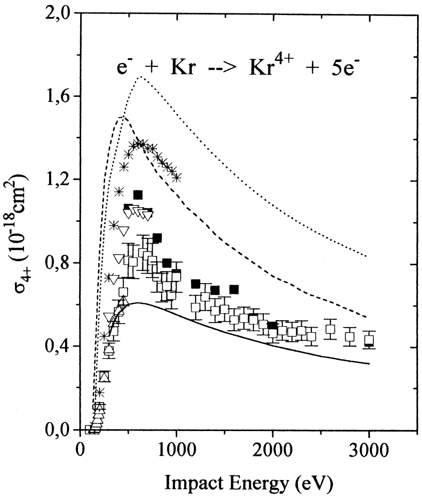

Fig. 4. Electron impact ionisation cross section σ_{4+} as a function of the incident energy. □ present data; + Stephan et al. [21]; * Krisnakumar and Srivastava [26]; △ Syage [27]; ■ Schram [25]; ··· Fisher et al. [7]; — Shevelko and Tawara [8]; --- Deutsch et al. [9].

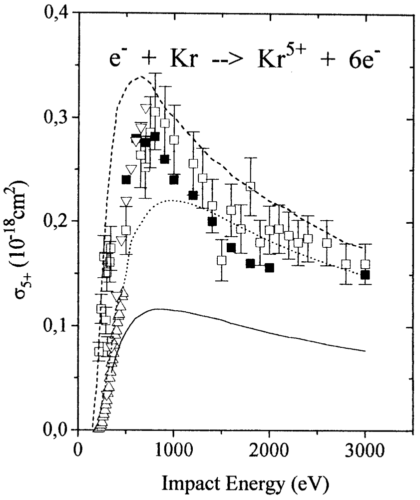

Fig. 5. Electron impact ionisation cross section σ_{5+} as a function of the incident energy. □ present data; △ Syage [27]; ▽ Lebius et al. [28]; ■ Schram [25]; — Shevelko and Tawara [8]; --- Deutsch et al. [9].

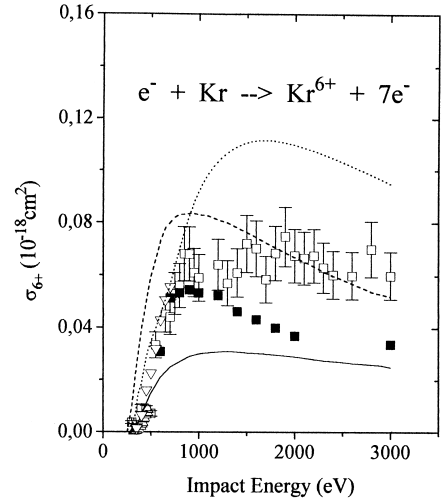

Fig. 6. Electron impact ionisation cross section σ_{6+} as a function of the incident energy. □ present data; △ Syage [27]; ▽ Lebius et al. [28]; ■ Schram et al. [25]; · · · Fisher et al. [7]; — Shevelko and Tawara [8]; --- Deutsch et al. [9].

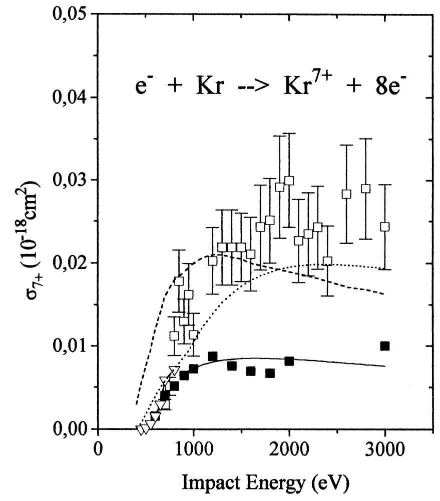

Fig. 7. Electron impact ionisation cross section σ_{7+} as a function of the incident energy. □ present data; ▽ Lebius et al. [28]; ■ Schram et al. [25]; · · · Fisher et al. [7]; — Shevelko and Tawara [8]; --- Deutsch et al. [9].

originally derived for the single ionisation of an atom by electron impact [10], to atomic multiple ionisation. In the case of the formation of highly charged rare gas ions the semiempirical fitting procedure used in the DM formalism was slightly modified [9]. Using this modified fitting procedure, we were able to calculate cross sections for the formation of Kr^{n+}. Fisher and colleges, based on observed scaling laws of MICS by electron impact, have proposed expressions for calculating the cross sections for several atoms and ions. The formula obtained by Fisher et al. [7] was derived using the minimal energy required for the extraction of n electrons from the target ground state, and as the authors mentioned, the accuracy is within a factor of 2 for most of the experimentally studied multiple ionisation cross sections.

Fig. 2 shows the cross section σ_{2+} for impact energies up to 3000 eV. The present results are in good agreement both in slope and magnitude with values from [20–22 and 25–28] considering the associated experimental uncertainties.

σ_{3+} are shown in Fig. 3. The present results are in good agreement both in slope and magnitude with values from Nagy et al. [20], and they are 10% higher than the values from Syage [27]. Results from Fisher et al. [7] are in good agreement within the associated uncertainties for most of the experimental data available in the literature. The results from Krisnakumar and Srivastava [26] are systematically 20% higher than the present results. Theoretical values from the ST expression [8] are lower than the measured cross sections by approximately 20%.

For $n = 4$, Fig. 4, discrepancies are observed near the resonance region. The present results show 40% difference to the data of Krishnakumar and Srivastava [26] and a 6% difference relative to the results of Syage [27] and of Schram [25]. For impact energies higher than 600 eV the agreement is satisfactory. The calculated values from DM formalism [9] exceed our experimental data by about 45%, whereas the expression from [7] gives results about two times the present data. Calculated values based on the ST expression [8] are lower than the measured cross sections by about 20%.

Figure 5 shows the cross sections for $n = 5$. The agreement between our measurements, those of Schram [25], Syage [27], and Lebius et al. [28] is good considering the combined uncertainties. In the theoretical aspect, agreement with the DM formalism [9] and Fisher et al. [7] is excellent, but the ST expression [8] underestimates the cross sections by about a factor of 2.

For σ_{6+}, presented in Fig. 6, our results show good agreement below 700 eV with the data from [25] and the data from [28]. However, beyond this energy there is a clear disagreement both in absolute values and in slope between the present data and the only other measurements available in the literature [25]. The calculated values from the DM formalism [9] basically differ from our results in slope, whereas data from the expression of Shevelko and Tawara [8] are lower than the measured cross sections by about a factor of 3.5, although the slope is approximately the same. The expression from [7] overestimates our data by about a factor of 2.

For $n = 7$, Fig. 7, there is excellent agreement between our data and those of Schram [25] and Lebius et al. [28] up to 900 eV. However, the present results are about two times higher than the values reported in [25]. Again, the calculations using the DM formalism [9] were able to predict our absolute results, however the position of the maximum is not the same. The values based on the ST formalism [8] are lower than the measured cross sections by approximately a factor of 3.5. The results from [7] are in good agreement with our data.

3.2. Fano-Bethe plot

The asymptotic expression for electron collision cross sections derived for energies higher than the maximum cross section, was fitted to the Kr^{n+} data and is displayed in the form of a Fano-Bethe plot in Fig. 8. Our results for Kr^{n+}, with $n = 2$–7 are shown to be proportional to ln E/E, for the region higher than the maximum, confirming that the reactions are strongly dominated by optically allowed processes. No Auger features have been observed in the spectra for the energy range studied.

In [29] an empirical model was proposed, which describes the dependence of the integrated oscillator strength for multiple ionisation in terms of the final ionic charge state, n. M_n^2 is shown to decrease monotonically with increasing number of ejected electrons having an exponential behaviour modulated by a power dependence. The model contains four adjustable parameters, which depend on the gas considered, allowing predictions to be made for highly stripped ionisation reactions. The minimum ionisation potential was obtained from [30].

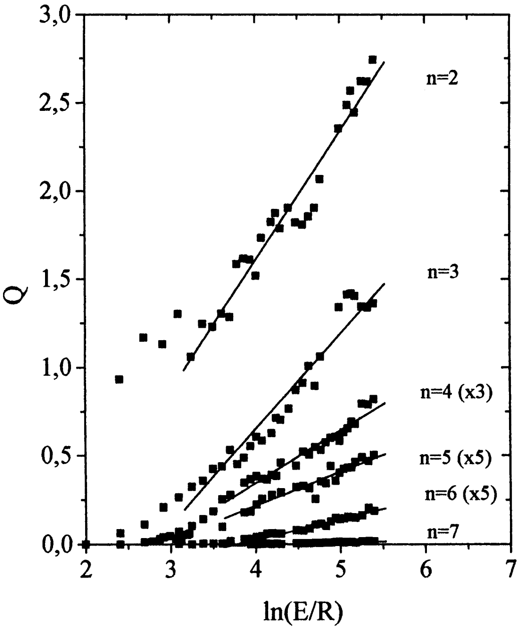

Fig. 8. Fano-Bethe plot for the process e + Kr ⇛ Kr^{n+} + $(n + 1)e$. The quantity Q is defined as $\sigma_{n+}E/(R\ 4\pi a_o^2)$.

The integrated oscillator strengths for Kr^{n+} (M_{n+}^2) are presented in Fig. 9 with previously reported values. In the case of Kr, as far as we know, the only IOS determined for multiple ionisation in the literature are from Schram [25]. The accuracy of these values is about 20%. Our results compare well with those previously reported by Schram and in spite of the differences among the absolute values the present estimation follows the general trend.

3.3. The apparent threshold energies

We determined the apparent threshold energy of multiple ionisation of krypton for $n = 3$–7. The threshold is taken considering the intercept of linear least-squares fits of the experimental data, below the maximum region in the cross section plot and the

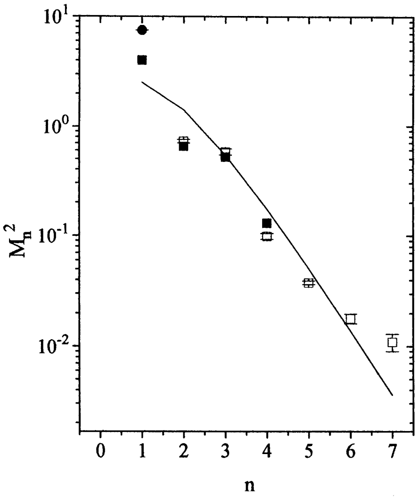

Fig. 9. Integrated oscillator strength (M_n^2) as a function of the number of ejected electrons. □ present data; ● Schram et al. [23]; ■ Schram [25]; — empirical expression from [29].

impact energy axis. The result of this extrapolation is presented in Fig. 10 with data from [22,30,31].

The energy scale was checked by linear electrostatic analysis [16] as mentioned earlier. Although the energy resolution (2 eV) of our experiment is not high, the threshold values are in good agreement with the spectroscopic data, except for $n = 7$ where our data is 50% higher.

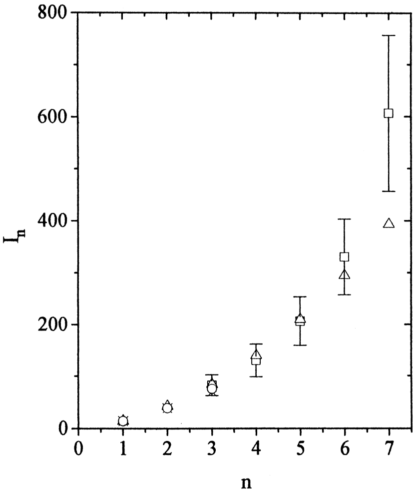

Fig. 10. Measured threshold energies as a function of the incident energy. □ present data; × Wetzel et al. [22]; △ [30]; ○ Winter et al. [31].

4. Conclusions

The present result for σ_{n+} with $n = 2$–5 for krypton shows reasonable agreement with the previous measurement in the literature. The ionisation cross sections for the formation of Kr^{6+} and Kr^{7+} reported here present important discrepancies to data from [25] for impact energies higher than the peak region. This disagreement exceeds the maximum combined experimental uncertainties. There is no clear explanation of this discrepancy.

Further research into this area is required on both the experimental and theoretical levels. Improved resolution (and intensity) would allow more accurate measurements of MICS. More results are also desirable from the photoionisation complimentary experiment.

Acknowledgement

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