The ionization of Li^+ to Li^{3+} by electron impact

B. PEART and K. T. DOLDER
Department of Atomic Physics, University of Newcastle upon Tyne
MS. received 16th May 1969

Abstract. The crossed-beam method for measuring electron impact ionization cross sections of ions has been developed so that very small cross sections ($\sim 10^{-21}$ cm^2) can now be determined with an accuracy approaching $\pm 10\%$. The reaction $Li^+ + e \rightarrow Li^{3+} + 3e$ has been investigated for incident electron energies between threshold (198 ev) and 2·5 kev. The cross section reached a maximum value of $1{\cdot}04 \times 10^{-20}$ cm^2 and fell to $4{\cdot}5 \times 10^{-21}$ cm^2 at 2·5 kev. The results are discussed and compared with theoretical and experimental values for the double ionization of helium.

1. Introduction

Multiple ionization by electron impact has not been extensively studied, and almost all of the theoretical work has been confined to the double ionization of helium. Geltman (1956) calculated the s-wave contribution for helium so that his results are likely to be valid only near threshold. Ionization by fast electrons was discussed by Mittleman (1966) who considered two possible mechanisms. In the first, an incident electron initially causes single ionization and the two outgoing electrons may then produce further ionization within the same atom. This process is likely to be significant only for large atoms and can be disregarded for helium. In the second mechanism, the projectile initially removes one electron from helium in a time which is much shorter than the orbital period. Consequently the remaining electron is not in an eigenstate of the ion and there is some possibility that it may make a transition to the continuum. For fast electrons, in the limit of Bethe's approximation, this argument predicts that the ratio of cross sections for single and double ionization (σ_+/σ_{++}) is a constant, which Mittleman calculated to be 198 for helium.

Byron and Joachain (1966) subsequently considered the effects of electron correlation in helium and pointed out that the value obtained for the ratio σ_+/σ_{++} should depend very critically on the choice of wave functions. It therefore seems that comparisons of theoretical and experimental results might provide an exceptionally stringent test of wave functions. These papers have been briefly reviewed by Rudge (1968).

McDowell and Coleman (1969) recently carried the discussion further. They argued that, *if* the Born series converges to its first term for all direct processes, the cross sections for multiple ionization by fast electrons will be given by the first Born approximation, provided that accurate correlated wave functions are used. However, for non-relativistic energies they suggested that the contributions from the first and second terms in the Born series might be comparable.

The present paper will describe measurements of cross sections for

$$Li^+ + e \rightarrow Li^{3+} + 3e \qquad (1)$$

for electrons with energies between threshold (198 ev) and 2·5 kev. This reaction is analogous to the double ionization of helium, but the experimental methods are very different. The results should therefore provide a sensitive and independent check for theories of the double ionization of two-electron systems.

2. Apparatus and method

The method was similar to that described by Dolder *et al.* (1961) and reviewed by Harrison (1966, 1968) and Dolder (1969, to be referred to as I). A pure beam of $^7Li^+$ ions was bombarded by an electron beam so that a small proportion ($\sim 10^{-12}$) of the Li^+ was ionized to Li^{3+}. The Li^+ and Li^{3+} ions were then separated, in a manner to be described below, and the respective beam currents, I^+ and I^{3+}, were measured. The cross section (σ_{++}) for reaction I is related to measurable quantities by

$$\sigma_{++} = \frac{I^{3+}}{I^+ J} \frac{eVv}{3(v^2+V^2)^{1/2}} F \tag{2}$$

where v and V represent the electron and ion velocities, J is the electron current and e is the electronic charge. The quantity F, which is computed from measured current density distributions in the colliding beams, takes account of non-uniformities in these distributions. Details of the derivation of equation (2) and the determination of F are given in the reviews which have been cited. Typical values for these experiments were, $I^+ \simeq 10^{-7}$ A, $I^{3+} \simeq 10^{-18}$ A, $J \simeq 10^{-3}$ A and the energy of the Li^+ ions was usually 2·0 kev.

It was necessary to make two developments to the apparatus previously used because the cross sections for reaction 1 are extremely small. Since the current of Li^{3+} ions formed by these collisions was usually less than 10^{-18} A, it could not be measured by an electrometer. The ions were therefore detected individually and counted. A second modification was required because the ratio of the currents I^+ and I^{3+} was sometimes as large as 10^{12}. Two stages of deflection were therefore needed to separate beams of such different intensities.

The ion detector is illustrated in figure 1. Essentially, it consisted of an 18 stage electron multiplier (E.M.I. type 9642) which was fitted with two additional electrodes (E1 and E2). The dynodes were venetian-blind shaped and made from beryllium copper. Electrode E1

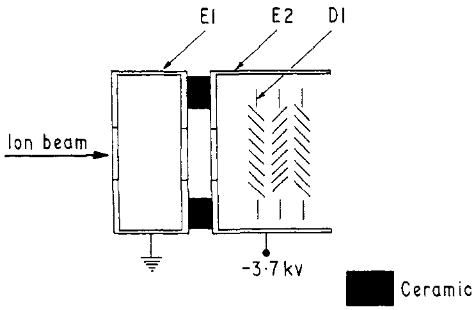

Figure 1. Initial stages of the ion detector. The first three dynodes of the multiplier and the two electrodes (E1 and E2) which were added to enhance the efficiency of the detector are shown.

was earthed but E2 was held at a potential 200 v negative with respect to the first dynode (D1). Its purpose was to prevent the loss of secondary electrons from the initial stages of the multiplier. The dynode potentials were arranged so that D1 was approximately 3·5 kv negative, whilst the final dynode was at earth potential. Consequently, Li^{3+} ions acquired an additional energy of about 10·5 kev on striking D1. The coefficient for secondary electron emission is large for such energetic ions and, since the loss of these electrons was small, the detection efficiency for Li^{3+} approached 100%. It was not possible to measure the efficiency for Li^{3+} ions but the following method was used to determine the efficiency of the detector for Li^{2+}.

The detector was used in a measurement of the cross section for

$$\mathrm{Li}^+ + \mathrm{e} \rightarrow \mathrm{Li}^{2+} + 2\mathrm{e} \tag{3}$$

which has previously been measured by Lineberger *et al.* (1966) and Peart and Dolder (1968, to be referred to as II). For incident electron energies of 500, 600 and 700 ev the results of the two previous experiments agree within 3%. A comparison of the averages of these results with the present measurements gave 96%, 96% and 97% for the efficiency of the detector for Li^{2+} at the three electron energies.

Slightly higher efficiencies might be expected for Li^{3+} ions because they gain more energy from the potential of the first dynode. The efficiency for Li^{3+} was therefore taken to be $96 \pm 4\%$. The efficiency for Li^{2+} was checked several times during the experimental programme and proved to be remarkably constant.

The efficiency of the detector has also been measured for Mg^{2+} and Mg^{3+} ions with initial energies of a few kev. This was done by comparing the count rate which a tenuous beam of these ions produced at the detector with the current ($\sim 10^{-15}$ A) measured by an accurate electrometer when the beam entered a Faraday cup. Efficiencies of $88 \pm 3\%$ and $89 \pm 3\%$ were deduced for Mg^{2+} and Mg^{3+}, respectively, from these measurements. This confirms the high efficiency of the detector and it is consistent with the result for Li^{2+}, because lighter ions, of given energy, tend to produce more secondary electrons and consequently their detection efficiency should be a little higher.

Preliminary attempts to measure cross sections for reaction 1 showed that the 60° sector magnetic field, which served as an analyser in previous experiments, was unable to separate the beams of Li^+ and Li^{3+} with sufficient resolution. A small fraction ($\sim 10^{-10}$) of the Li^+ beam, which was scattered from slit edges or residual gas, entered the particle detector and obscured the Li^{3+} beam. This problem was overcome by placing a 90° radial electric field E between the magnetic analyser M and the detector, as illustrated by figure 2. This

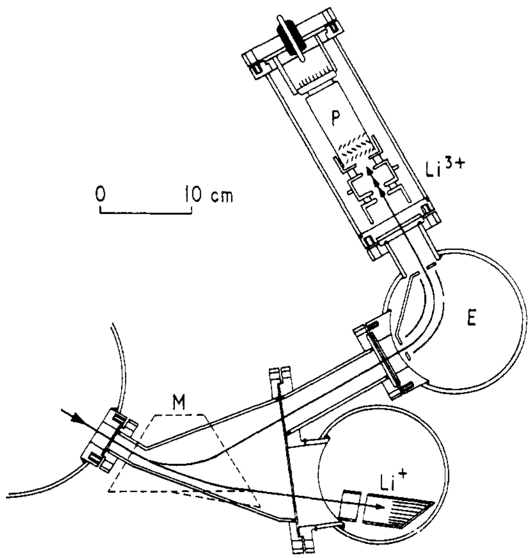

Figure 2. The two-stage analyser used to separate beams of Li^+ and Li^{3+} ions. The beams are first separated in the 60° sector magnetic field M so that the Li^+ ions are collected by a Faraday cup. The Li^{3+} ions subsequently pass through a second analyser E with a 90° radial electrostatic field. These ions are then detected by the signals they produce in a particle multiplier P.

two-stage analyser was very effective. When it was used, the signal due to ion scattering and all other extraneous processes, was about one count s^{-1}. This was, typically, a fifth of that due to reaction 1. The amplified electronic pulses due to each ion had an average height of about 10 v, but only 1 v discrimination was needed to suppress electronic noise.

Two alternative methods of beam modulation were used to separate the signals due to reaction 1 from those caused by extraneous processes. Results obtained with these methods will be represented by the closed and hollow circles in figure 4. The two methods have already been reviewed in detail, and they are respectively illustrated by figures 6 and 7 of the article by Harrison (1968) and figures 5–2–6 and 5–2–7 of I.

Care was taken to ensure that the proportion of ions of a given type and energy, which passed through the two-stage analyser (to be called the 'transmission efficiency') was virtually 100%. Transmission efficiencies were measured for Li^+, Mg^+ and Mg^{2+} ions.

In all cases they were found to be very insensitive to the potentials applied to the cylindrical electrodes of the electrostatic analyser, and never less than 99%. It follows that the efficiency of the detector was not sensitive to the region of the first dynode which was struck by the incident beam and this was achieved by mounting the multiplier with the slats of its dynodes horizontal.

3. Experimental checks

The results of four checks are illustrated by figure 3. Figure 3(*a*) shows that the cross section of reaction 1, measured for 600 ev electrons, did not depend upon the ion energy.

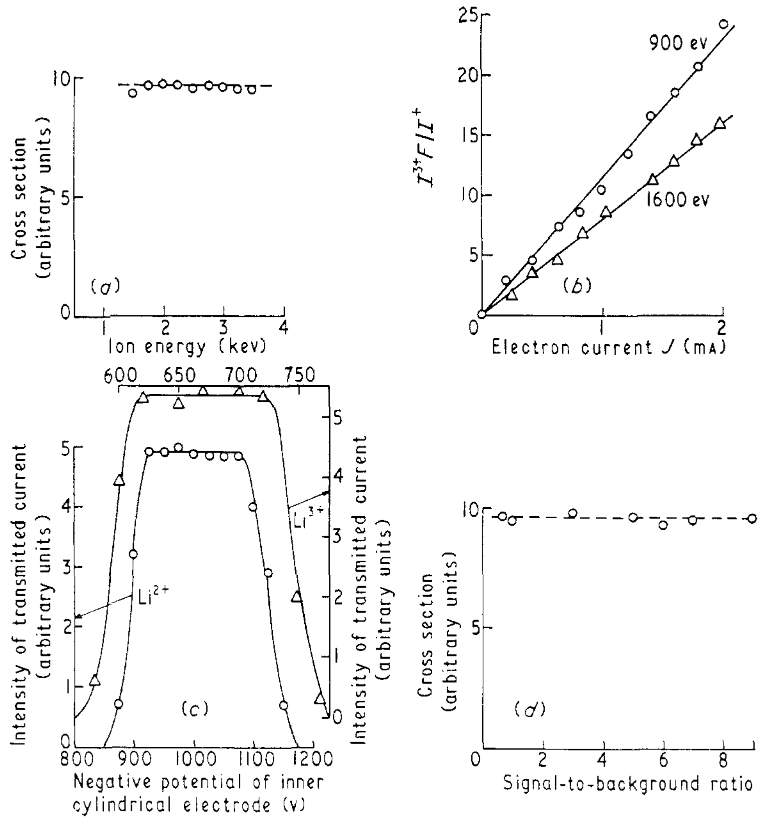

Figure 3. Results of experimental checks. (*a*) Invariance of the measured cross section with ion energy. (*b*) Two examples of the linear relation observed between $I^{3+}F/I^{+}$ and the electron current J. (*c*) These curves illustrate the insensitivity to electrostatic analyser potential of the transmission and detection efficiencies of Li^{2+} and Li^{3+} ions. (*d*) Invariance of the measured cross section with signal to background ratio.

A second check follows from equation 2 which implies that, for constant electron and ion velocities, the cross section should be proportional to the gradient of a line obtained by plotting $I^{3+}F/I^{+}$ against the electron current J. Two examples of these linear relations, which were measured for electron energies of 900 and 1600 ev, are illustrated by figure 3(*b*). The observed linearity, and the fact that both lines pass through the origin, show that a number of potential sources of error were absent. Figure 3(*c*) illustrates the invariance of the transmission efficiencies of Li^{2+} and Li^{3+} ions with the negative potential applied to the inner electrode of the cylindrical analyser, whilst figure 3(*d*) demonstrates that the measured cross section was independent of the signal-to-background ratio. The signal-to-background ratio, which is the count rate of Li^{3+} ions formed by reaction 1 divided by that due to all extraneous processes, was varied by changing the residual gas pressure in the apparatus. During most experiments the signal-to-background ratio was between 3 and 5. These checks give confidence that the results to be presented in § 4 were not significantly affected by the types of error which have previously been encountered in crossed beam experiments. A discussion of errors and checks in this type of experiment will be found in I.

A further, and particularly important check, is to ensure that the measured cross section is zero below threshold. It will be seen in the following section that this was true for the present experiment.

4. Results and discussion

Figure 4 shows measurements of the cross section σ_{++} for reaction 1 plotted against the energy E of incident electrons. The error bars denote 90% confidence limits of random error at each energy and the hollow and closed circles refer to experiments in which the alternative beam modulation systems, identified in § 3, were used. It can be seen that there were no significant differences between results obtained by the two methods.

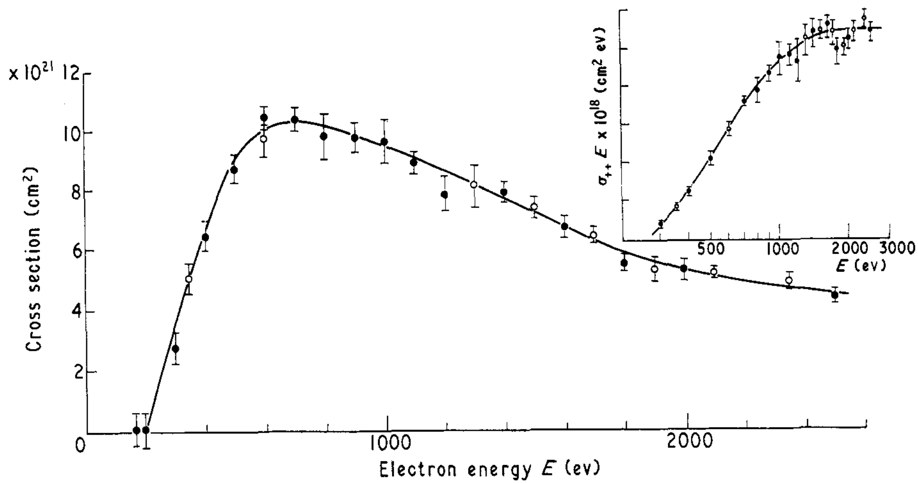

Figure 4. Measured cross sections σ_{++} for the double ionization of Li^{2+} ions. The inset shows $\sigma_{++}E$ plotted against the electron energy E on a logarithmic scale. The hollow and closed circles denote results which were obtained with the modulation methods identified in the text.

The present results, and the 90% confidence limits at each energy are listed in table 1. The systematic errors were estimated to be less than $\pm 9\%$ and this included the uncertainty in the detector efficiency. The method used to estimate errors was described in detail by Wareing and Dolder (1967).

The inset of figure 4 shows $\sigma_{++}E$ plotted against lg E. This result is qualitatively quite different from that found for single ionization (see II) but it resembles the curve for the double ionization of helium published by Schram *et al.* (1966). It seems that, at high energies, σ_{++} is at least roughly proportional to E^{-1} for both helium and Li^+.

Mittleman, and Byron and Joachain compared the results of their calculations with the ratio σ_+/σ_{++} of cross sections measured for the single and double ionization of helium. For fast electrons, they predicted that this ratio should be independent of the incident electron energy. Mittleman obtained $\sigma_+/\sigma_{++} = 198$ for helium and Moores (1969, private communication) showed that these equations give a ratio 350 for Li^+. The ratios (σ_+/σ_{++}) for Li^+ are shown in this way by the crosses in figure 5 for which values of σ_+ for Li^+ were taken from II. The hollow circles represent the same ratios for helium which were measured by Schram *et al.* (1966). Qualitative similarities between the two sets of results are apparent, but in neither case does the ratio tend to a constant at high energies as predicted by theory.

Table 1.

Electron energy (ev)	Cross section (10^{-21} cm²)	Random error (±%)
300	2·75	20
350	5·1†	10
400	6·5	8
500	8·7	7
600	10·4	7
600	9·7†	7
700	10·4	4
800	9·8	8
900	9·8	4
1000	9·6	8
1100	8·9	5
1200	7·8	9
1300	8·2†	8
1400	7·9	5
1500	7·4†	5
1600	6·8	5
1700	6·5†	4
1800	5·6	6
1900	5·4†	9
2000	5·3	8
2100	5·2†	4
2350	5·0†	5
2500	4·5	6

† These results were obtained with the beam technique illustrated by figure 5–2–6 of paper I. The remaining points were obtained with the technique represented by figure 5–2–7 of the same paper. Systematic errors are less than ±9% for all electron energies.

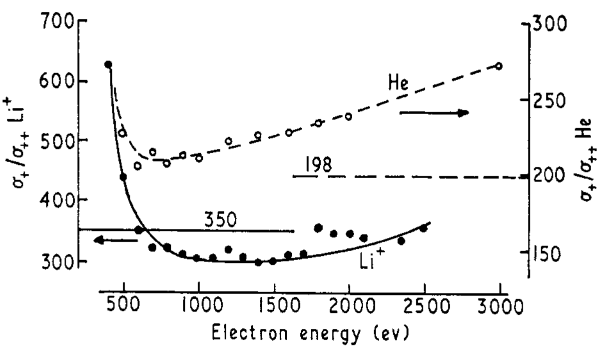

Figure 5. Ratios of cross sections for single and double ionization of Li$^+$ and helium plotted against electron energy. Constant ratios predicted by Mittleman's approximation are shown in each case.

If new theoretical methods are evolved to improve the understanding of multiple ionization, the results presented in figure 5 should serve as two sensitive and independent checks. At the higher electron energies used in the present experiments, the incident electron could probably be accurately represented by a plane wave which should not be significantly distorted by the initial coulomb field of Li$^+$.

Acknowledgments

This work was supported by the Science Research Council who also provided a studentship for one of us (B.P.).

References

Byron, F. W., and Joachain, C. J., 1966, *Phys. Rev. Lett.*, **16,** 1139–42.
Dolder, K. T., 1969, *Case Studies in Atomic Collisions,* Ed. E. W. McDaniel and M. R. C. McDowell (Amsterdam: North Holland), Chap. 5.
Dolder, K. T., Harrison, M. F. A., and Thoneman, P. C., 1961, *Proc. R. Soc.* A, **264,** 367–8.
Geltman, S., 1956, *Phys. Rev.*, **102,** 171–6.
Harrison, M. F. A., 1966, *Brit. J. Appl. Phys.*, **17,** 371–81.
—— 1968, *Methods of Experimental Physics* **7A,** Ed. B. Bederson and W. L. Fite (New York: Academic Press).
Lineberger, W. C., Hooper, J. W., and McDaniel, E. W., 1966, *Phys. Rev.*, **141,** 151–7.
McDowell, M. R. C., and Coleman, J., 1969, *An Introduction to the Theory of Electron Ion Collisions* (Amsterdam: North Holland).
Mittleman, M. H., 1966, *Phys. Rev. Lett.*, **16,** 498–9.
Peart, B., and Dolder, K. T., 1968, *J. Phys.* B (Proc. Phys. Soc.), [2], **1,** 872–8.
Rudge, M. R. H., 1968, *Rev. Mod. Phys.*, **40,** 564–90.
Schram, B. L., Boerboom, A. J. H., and Kistemaker, J., 1966, *Physica,* **32,** 185–96.
Wareing, J. B., and Dolder, K. T., 1967, *Proc. Phys. Soc.*, **91,** 887–93.