

Absolute electron impact ionization cross sections of Li in the energy range from 100 to 2000 eV

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The absolute electron impact ionization cross sections for lithium in the energy range between 100 and 2000 eV were measured by the nonmodulated crossed beam technique. The neutral lithium beam is produced by a Knudsen cell and crossed at right angles with the electron beam. The ions formed are collected on a plate and their intensity determined with a dc amplifier. The neutral beam is condensed on a cold trap cooled with liquid nitrogen, this temperature being much lower than that required to obtain total condensation. The amount of metal deposited is measured by the isotopic dilution technique and by atomic absorption, and the density of the atoms in the neutral beam is calculated. The total absolute ionization cross sections can then be determined. All possible errors have been carefully analyzed and their magnitudes estimated. The absolute ionization cross section for Li at an energy of 500 eV is $Q_{\text{Li}} = 0.358 \times 10^{-16} \text{ cm}^2$. This value is half of that obtained by McFarland and Kinney. The partial ionization cross sections for the singly and doubly charged ions, is determined with a mass spectrometer attached to this apparatus. For the singly charged ions, the variation of the cross section with the energy of the ionizing electrons is in agreement with the optically allowed transition law $Q = A \log BE/E$. From the variation of Q with E , the squared matrix element of the transition moment $|M|^2$ is determined. New calculations of the ionization cross section of Li were performed in the framework of the Born-Bethe approximation as modified by Gaudin and Botter to take into account collisions with large momentum variation of the incident electron. Hartree-Fock type wavefunctions for the ground state atom (tabulated by Clementi) were used. The calculated values are in good agreement with our experimental results and with the former theoretical results calculated by various methods. This work also indicates that the experimental results of McFarland and Kinney for Li are too large.

I. INTRODUCTION

Relative electron impact ionization cross sections for lithium have been measured by Brink¹ with a crossed beam technique. Using the same arrangement McFarland and Kinney^{2,3} have performed the only absolute measurements in the energy range of interest. Other absolute determinations have been made by Aleksakhin^{4,5} in the threshold region.

The comparison of theoretical and experimental ionization cross sections for alkali metals and particularly for Li and Na has been discussed in detail by McDowell.⁶ The experimental results are generally twice as large as the calculated ones. Only one theoretical curve of Omidvar⁷ is in agreement with the measurements of McFarland. Recent calculations⁸ by the first author in the range of validity of the Born approximation however agree with the other more or less sophisticated theoretical calculations in the frame of the same approximation by Peach,⁹ McDowell,^{6,10} and Gaudin.¹¹

McDowell arrived at the conclusion that for Li the experimental results of McFarland and Kinney could be 50% too large in the energy range above 200 eV. The greatest absolute error in their experiments may arise from the determination of the intensity of the neutral beam with a surface ionization detector. The authors assumed 100% efficiency

for oxidized tungsten but this may not be true for Li.

Since a discrepancy of a factor of two is observed between the calculated and the experimental results, new measurements were performed in order to obtain reliable absolute electron impact ionization cross sections of lithium in the energy range from 100 to 2000 eV. The density of the atomic beam was measured using a condensation technique in order to avoid the difficulties of surface ionization. Kieffer and Dunn¹² have listed in their review article, the instrumental factors which might cause systematic errors in the absolute cross section measurements. In the present work all the instrumental sources of error were checked and the systematic errors carefully estimated.

II. APPARATUS AND PROCEDURE

A schematic diagram of the apparatus is shown in Fig. 1. The Knudsen cell, the collision chamber and the mass spectrometer are placed in three different compartments which are pumped differentially by mercury diffusion pumps. The first compartment is connected to the second one via the definition hole of the atomic beam. The electron gun, the collision chamber, two movable slits for the definition of the atomic beam and the neutral beam collector are located in the second compartment. This part of the apparatus and the mass spectrom-

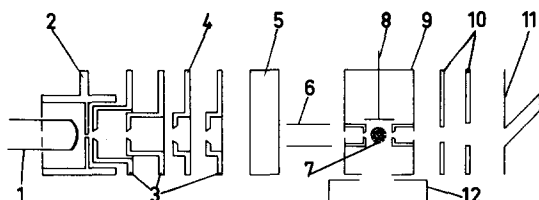


FIG. 1. Schematic diagram of the apparatus. 1, Filament, 2, Wehnelt, 3, accelerating anodes, 4, Focusing anodes, 5, vertical deflectory plates, 6, horizontal deflectory plates, 7, molecular beam, 8, ion collector, 9, collision chamber, 10, diaphragm, 11, electron beam collector, 12, electric shields.

eter are connected only through the definition slit of the ion beam. The mass spectrometer itself is a 20 cm radius, 60° magnetic deflection instrument. The collector is equipped with both a movable Faraday cup and a secondary electron multiplier. During the experiments the background pressure was always of the order of 10^{-6} torr in compartment 2 and lower than 10^{-6} in the mass spectrometer. In the Knudsen cell region the pressure was lower than 10^{-5} torr.

A. Electron Gun and Collision Chamber

A schematic diagram of the electron gun is shown in Fig. 2. The electrodes and the collision chamber are made of stainless steel. Vertical and horizontal deflection plates are used in order to obtain a well centered beam in the collision chamber, thus avoiding reflection of some electrons on the walls of the chamber. The electron current is of the order of $1 \mu\text{A}$ at 100 eV and reaches $15 \mu\text{A}$ at 3000 eV energy. The ion collector is connected to a dc total feedback amplifier and is always at a potential near zero during the total collection experiments. A weak positive potential is applied to the collision chamber to ensure total collection of the ions produced. The collection efficiency versus drawout potential is shown in Fig. 7. Above 6 eV, the ion current reaches a plateau and the collection may be considered as total. Further details will

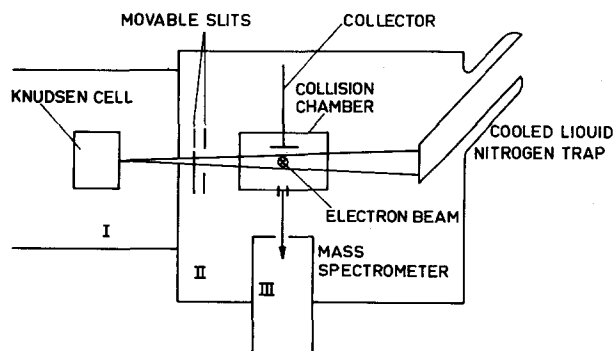


FIG. 2. Electron gun and ionization chamber.

be given in the discussion of the errors. The atomic beam passes through very large apertures in the collision chamber.

B. Neutral Atomic Beam and Intensity Measurements

A resistance heated Knudsen cell is used to produce the atomic beam (see Fig. 1). The cell can be moved in two directions in order to obtain a well centered beam in the collision chamber. The effusion hole of the cell has a diameter of 0.5 mm. The temperature is measured with a chromel alumel thermocouple very close to the hole.

The neutral beam enters the second compartment through a 2 mm diameter hole. After the collision chamber the beam is collected on a liquid nitrogen cooled tantalum plate. After each experiment the collector is taken out and the amount of deposited material determined using an isotope dilution technique or by atomic absorption spectroscopy (see Sec. II C).

Several experiments were performed in order to study the condensation conditions of atomic beams of alkali metals, especially Li. The apparatus is shown schematically in Fig. 3. The neutral beam impinges on a plate at an incident angle of 45° . The temperature of the collector plate can be varied from -100°C to $+50^\circ\text{C}$. A hot tungsten filament is situated one centimeter away from the neutral beam collector and an ion collector is placed near the filament. A fraction of the reflected atoms falls onto the hot filament and the ions produced are measured.

In Fig. 4 the variation of the ion intensity versus temperature is given. At -50°C only one percent of the intensity measured at high temperature is still observed, and therefore one can assume that not more than 1% of the atomic beam is reflected at this temperature. Three different metals were used as collectors. On gold and tantalum the results are similar, while tungsten appears to be less efficient. Tantalum was chosen for the present experiments.

C. Experimental Procedure

Before each run, the sample is heated in the Knudsen cell for 10 hours at 500°C and under op-

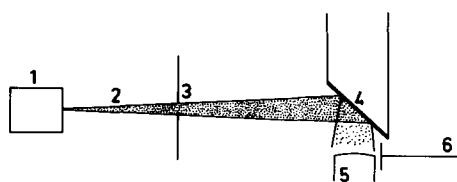


FIG. 3. Experimental arrangement for the study of the condensation conditions. 1, Knudsen cell, 2, molecular beam, 3, diaphragm, 4, neutral atomic beam collector, 5, filament, 6, ion collector.

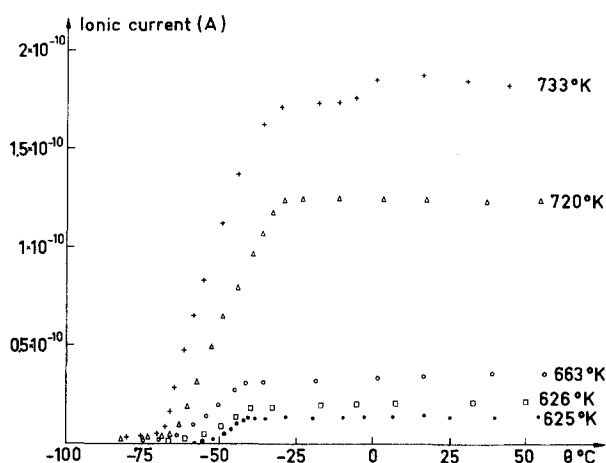


FIG. 4. Condensation efficiency of Li on Tantalum as a function of the temperature of the neutral beam collector.

erating conditions for at least two hours. One of the plates of the movable slits is used as a shutter and it kept closed during these preliminary operations. When the pressure in the first chamber is less than 10^{-5} torr, the shutter is opened.

First the composition of the neutral beam is studied with the mass spectrometer using the collision chamber as the ion source, the chamber being raised to a high positive voltage (4000 V). Then, the potential is lowered to a few volts (5 to 10 V), the collector is connected to the dc amplifier and the electron gun switched to negative voltage, this latter voltage being variable in order to measure the absolute cross sections at different electron energies.

The electron current is measured with a galvanometer and the ion current with a dc amplifier. Different high value resistors of the order of 10^{10} to $10^{11} \Omega$ were used. The ion current from the neutral beam is always measured as the difference between the currents with and without the beam in order to deduce the actual background.

Throughout an entire run the atomic beam is collected on the cold trap and the time measured. After the experiment, the collector is taken out and the material deposited is dissolved in a known amount of acidified water. An aliquot of the solution is mixed with a given amount of a solution of a pure isotope (^6Li in these experiments) and then analyzed by mass spectrometry. The weight of deposited material can be calculated from the isotopic composition.¹³ In the atomic absorption spectroscopy measurements, the absorption of the actual solution is compared to the absorption of reference solutions of known concentration and the actual concentration determined by interpolation.¹⁴ The two techniques give the same results to within the experimental error.

The amount of deposited material varies from 50 μg to 150 μg depending on the temperature of the cell and the duration of the run.

The mass spectrometer technique was used with pure lithium isotopes in order to check the errors in the collection device. No contamination was observed.

III. ABSOLUTE TOTAL IONIZATION CROSS SECTIONS

A. Determination of Cross Sections

The total ionization cross section at an electron energy E is given by

$$Q(E) = Q_1(E) + 2Q_2(E) + 3Q_3(E),$$

$$Q(E) = I_i t \bar{v} \pi l F / 4 N I_e,$$

where $Q(E)$ is the total ionization cross sections, $Q_1(E)$, $Q_2(E)$, ... single, double, ... ionization cross section, N is the total number of Li atoms in the neutral beam during the experiments, t is the time of exposure of the atom collector to the lithium beam, l is the diameter of the neutral beam in the interaction region, and \bar{v} is the average velocity of the atoms in the neutral beam.

$$\bar{v} = \frac{3}{4} \sqrt{2RT/M}.$$

F is a correction factor due to the inhomogeneities of the two beams

$$F = \int_0^l J_t(z) dz \int_0^l J_e(z) dz / \int_0^l J_t(z) J_e(z) dz,$$

where $J_t(z)$ and $J_e(z)$ are the spatial distributions of the neutral target beam and the electron beam along the z axis perpendicular to the plane of the beams. If either $J_t(z)$ or $J_e(z)$ is uniform, F becomes unity.¹² This is the case for the atomic beam (see Sec. III C).

B. Results

The preliminary results given in an earlier report¹⁵ were obtained before a mass analysis of the atomic beam had been carried out. The study of the composition of the atomic beam showed that some impurities were present, particularly H_2 and CO . The H_2 content was always low and it had very little effect on the ionization cross section of Li ($\sigma_{\text{H}_2} \approx \sigma_{\text{Li}}$) but the CO content was variable from one experiment to another and its ionization cross section is very large compared to that of Li (about 5 times larger).¹⁶

The mass spectrometric analysis gives the relative concentration of CO in the Li beam and the lithium ionization cross section can be deduced from the experimental results. In the total collection measurements, the ion intensity can be written

$$I_i = I_{\text{Li}} + I_{\text{CO}}.$$

The known density is n_{Li} (number of Li atoms per cc in the beam), therefore

$$Q_t = Q_{Li} + [n_{(CO)}/n_{(Li)}]Q_{CO},$$

where Q_t represents the cross section calculated with the measured intensity I_t and the density n_{Li} ; $n(CO)/n(Li)$ is proportional to $\rho(CO/Li)$, the mass spectrometric ratio of the ion currents.

The values obtained for Q_t in different experiments were plotted versus the ratio $\rho(CO/Li)$. The value extrapolated at $\rho(CO/Li) = 0$ for a given energy gives $Q_{Li}(E)$. In Fig. 5, four curves at different electron energies are shown. The experiments were performed under different conditions: oven temperature from 650 to 710 °C, exposure time from 2 to 5 hours, electron current from 0.5 μA to 2.5 μA at 600 eV energy. At high CO content the results are not reproducible.

The absolute ionization cross sections of Li at different electron energies are given in Table I and Fig. 10.

According to the Bethe formalism the ionization cross section at high energy is given by

$$Q(E) = A \log BE/E,$$

where A is proportional to the squared dipole matrix element $|Mi|^2$ of the given atom.

The value of $|Mi|_{Li}^2$ can be deduced from the $Q_{Li}(E)$ results. However in this case, the effect of the CO content on the measured squared matrix element is very large, $|Mi|_{CO}^2$ being 20 times larger than $|Mi|_{Li}^2$ (about 6 and 0.3, respectively). Therefore instead of taking the value of $|Mi|_{Li}^2$ from the extrapolated cross section which leads to a value of $|Mi|^2 = 0.45$, $Q \cdot E$ versus $\log E$ is plotted for different experiments with various CO contents, and from the diagram of $|Mi|_{exp}^2$ versus $\rho(CO/Li)$, $|Mi|_{Li}^2$ is deduced (see Fig. 6).

In fact $|Mi|_{exp}^2$ is not a rigorously linear function of $\rho(CO/Li)$ because $B(exp)$ in

$$Q_t = A_{(exp)} \cdot \log(B_{exp} \cdot E)$$

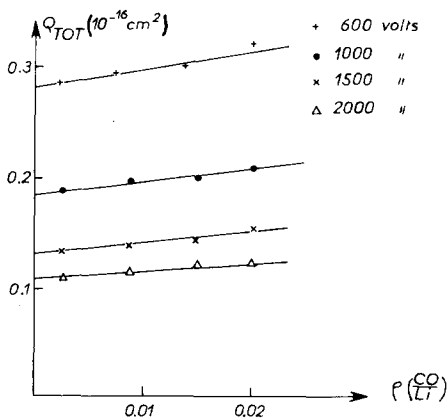


FIG. 5. Variation of the absolute ionization cross section as a function of the relative CO content of the neutral beam.

TABLE I. Single and double ionization cross section of lithium.

Energy	Q_1^+	Q_2^+
100	$1.0 \cdot 10^{-16} \text{ cm}^2$	
200	0.76	
300	0.57	$1.8 \cdot 10^{-19} \text{ cm}^2$
400	0.435	1.75
500	0.358	1.73
600	0.294	1.49
700	0.26	1.27
800	0.232	1.10
900	0.205	0.99
1000	0.19	0.88
1100	0.172	0.81
1200	0.158	0.74
1500	0.13	0.59
2000	0.103	0.44

varies with $\rho(CO/Li)$. However at $\rho = 0$, $|Mi|_{exp}^2 = |Mi|_{Li}^2$. The linearly extrapolated value is

$$|Mi|_{Li}^2 = 0.35 \pm 0.2.$$

C. Discussion of Errors

Necessary conditions for obtaining accurate ionization cross sections have been listed by Kieffer and Dunn in their review article.¹² The different points related to this experiment were taken from their publication. These are enumerated in Table II and will be discussed below.

1. Ion Current I

(a) As shown in Fig. 7, above 6 eV the collection efficiency of the ion current versus ion drawout potential reaches a plateau. With the ions of interest being formed in the atomic beam which is much narrower than the collision chamber, one can assume a 100% collection efficiency above 5 V/cm. The ion current is measured with a dc

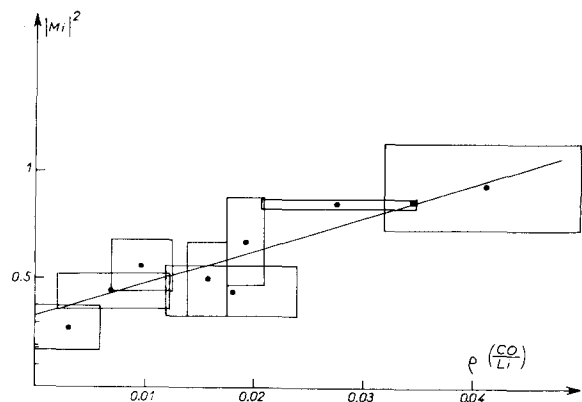


FIG. 6. Variation of the squared dipole matrix element as a function of the relative CO content of the neutral beam.

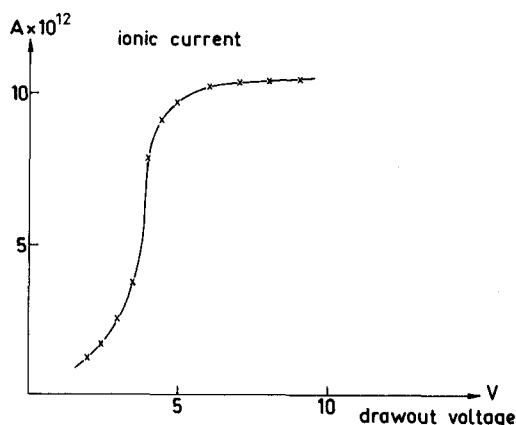


FIG. 7. Collection efficiency of the ions versus drawout voltage.

amplifier. The high value resistor was carefully calibrated. During the experiments the ion current was always lower than 10^{-11} A.

(b, c) In order to verify that no secondary electrons are emitted from the collector or that no ions are reflected, the fringe magnetic field of the mass spectrometer was used. The ion current was measured for different values of the magnetic field. No variation of the ion current was observed and the errors due to these effects are negligible.

(d) As discussed in the preceding paragraph impurities in the beam may produce spurious ions. This effect was taken into account for CO in the measurements and therefore does not introduce any systematic error. However, mass analysis has also shown that H_2 and Li_2 were present in the beam. The concentration of both molecules was lower than 1% and their collection efficiencies were not known. H_2 introduces a systematic error proportional to its concentration in the beam ($Q_{H_2} = Q_{Li}$). The effect of Li_2 is more subtle because Li_2 is taken into account in the density measurements while the number of ions depends on the relative cross sections of Li and Li_2 . If this latter value is exactly twice as large as that of the monomer, both errors cancel each other.

2. Electron Beam I_e

(a) With the electron gun described previously, a well-focused electron beam is obtained in the collision region. No current greater than 10^{-9} A is measured on the different defining electrodes and on the collision chamber walls. Therefore one can assume a total collection efficiency of the electron beam.

(b, c) No variation of the electron current is observed when the drawout potential of the electrons between the collision chamber and the collector is varied. As no current is observed on the electrode immediately preceding the electron trap, it is as-

sumed that no electrons are reflected, and that no secondary electrons are emitted from the trap.

(d) The current of secondary electrons emitted in the ionizing collision is proportional to the ion current (of the order of 10^{-11} A in the ionization chamber). Since the pressure is always very low in the apparatus, the number of secondary electrons produced in this way is negligible. Since no current is observed on the various electrodes of the electron gun, no secondary electrons are produced in collisions of the primary electrons with the defining apertures.

3. Target Beam

(a) The velocity of the lithium atoms in the beam is known from the oven temperature. The measurements are made with a thermocouple placed very close to the effusion hole. It is assumed that the temperature difference between the thermocouple and the atomic beam is less than 10°C . Moreover, since the diameter of the effusion hole is of the order of 0.5 mm and the pressure in the Knudsen cell is between 0.1 and 1 torr, one can assume that the beam is thermal. The largest error in the estimation of the velocity is less than 1% at 1000°K .

(b) The method used for the determination of the atomic beam flux was described previously. It was shown that below -50°C the collection efficiency of the alkali atoms on the cold trap is greater than 98%. Successive experiments with pure ^6Li and ^7Li showed that there is no measurable contamination during the experiments. It was also verified that the deposited material is completely dissolved during the treatment of the collector plate. The measurements of the concentration

TABLE II. Check points of the errors in the measurements.

Measured quantities	Check point
I_i	(1) Collection efficiency (2) Secondary electrons from the ion collector (3) Reflected ions from the collector (4) Spurious ion or electron currents
I_e	(1) Collection efficiency of the ionizing electron beam (2) Secondary electrons from the electron trap (3) Reflection of electrons from the trap (4) No collection of secondary electrons from ionizing collisions or from collisions with the defining apertures.
\bar{v}, N	(1) Velocity of target atoms in the beam (2) Accurate target beam flux determination (3) Inhomogeneities in the atomic and electron beams
L	(1) Length of the interaction region (2) Path length of the electron due to magnetic and electric fields.

either by isotopic dilution or by emission spectroscopy, introduce errors of the order of $\pm 2\%$.

(c) The electron beam is much narrower than the target beam (about 1 and 5 mm, respectively), and it is assumed to be homogeneous. Also, the homogeneity of the neutral beam is verified by moving the 0.2 mm slit perpendicular to the electron beam across the atomic beam. The ion current remains constant over the entire beam as can be seen in Fig. 8.

4. Electron Path Length

(a) Length of the interaction region. The diameter of the neutral beam is known from geometrical considerations, from the spot of the beam on the collector (which also gives the homogeneity of the beam) and from the homogeneity measurements (displacement of the slit). All these determinations are in agreement.

In order to verify that the electron beam is well centered in the atomic beam, the former is moved slightly across the latter (by means of the horizontal deflection plates) and positioned to give the maximum ion current at which point it is assumed that the beam is well centered. The error cannot be large because the position thus determined is almost identical with that fixed mechanically.

(b) The weak magnetic and ion drawout electric fields used in these experiments do not increase markedly the trajectories of the electrons at an energy greater than 100 eV, nor does the transverse electric field (5 V/cm) change the energy of the electrons by more than 1%. Summing up all the errors, they are estimated to be according to their source: Electron current $\Delta I_e/I_e = +1\%$, -3% , ion current $\Delta I_i/I_i = \pm 2\%$, density of the neutral beam $\Delta \rho/\rho = +4\%$, -5% , path length $\Delta L/L = \pm 7\%$. The total error is less than $+15\%$ and -20% .

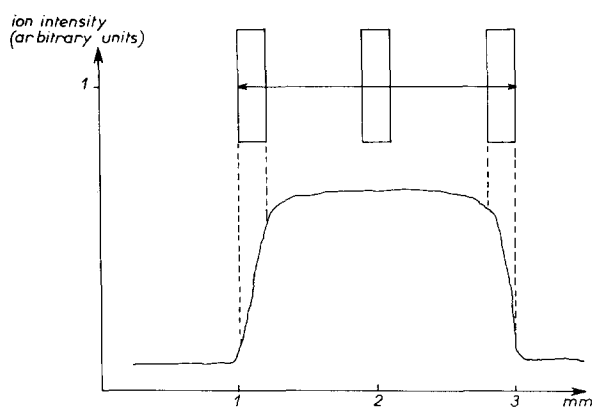


FIG. 8. Ion intensity versus position of the 0.2 mm movable slit when the slit is moved across the atomic beam parallel to the electron beam.

IV. PARTIAL IONIZATION CROSS SECTIONS

A. Partial Ionization Cross Sections

The partial ionization cross section measurements depend essentially on the relative efficiencies of the extraction of the ions from the source, the transmission of the mass spectrometer and the collection efficiency.

1. Mass Spectrometer

The definition slits used in these experiments were very wide, and the resolution of the mass spectrometer very low, 50, thus it is assumed that the transmission coefficients for the various ions are identical.

2. Collection Efficiency

Two types of collectors were used; a movable Faraday cup and a secondary electron multiplier. This made possible the determination of the multiplication factor of the multiplier for various types of ions.

However, in the case of lithium, this was only possible for the Li^+ ions, the Li^{2+} ion intensity (100 ions/sec) being too low to be measured with the Faraday cup. The multiplication factor is assumed to be the same for any type of ion of the same atom and given by¹⁷

$$MF = A(V - V_0),$$

where MF is the multiplier factor, V the velocity of the ion, V_0 threshold velocity for a given atom, and A a factor.

The multiplication factor was measured for different energies of the Li^+ ion and the same factor is assumed for Li^{2+} ions for the same velocity of both ions.

3. Extraction Efficiencies

The extraction efficiencies of the Li^+ and Li^{2+} ions from the ion source were measured for various drawout potentials and total accelerating voltages. The value obtained for the extrapolated value of the ratio $\text{Li}^{2+}/\text{Li}^+$ at $V = \infty$ (V being the accelerating voltage) is the same as the value obtained at 4 kV acceleration thus this effect can be neglected.

4. Experimental Procedure

Partial ionization cross sections were determined during the same experiments as the total cross section measurements.

The collision chamber and the electron gun are both raised to high positive potentials (+4 kV for the ionization chamber) and the ratio is measured with the electron multiplier and a dc amplifier.

B. Results

The results are shown in Table I. The Li^{2+}

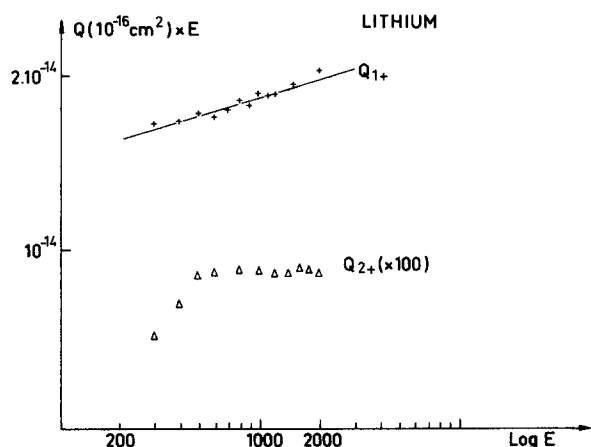


FIG. 9. Product of the absolute ionization cross section and the electron energy E as a function of $\log E$.

cross sections are always lower by a factor 200 than the Li^+ cross sections.

The largest error in these experiments is the determination of the multiplication factor for Li^{2+} ions. The error in the partial ionization cross section is estimated to be less than $\pm 15\%$. In Fig. 9, the values Q_1/E and Q_2/E versus $\log E$ are plotted. The value of $|Mi|^2$ for $Q_{(\text{Li}^+)}$ and for the total ionization cross section are the same, $Q_{(\text{Li}^{2+})}$ being negligible. We see also that $Q_{(\text{Li}^{2+})}$ follows a forbidden law. This is inevitable since no Auger process can lead to Li^{2+} .

V. DISCUSSION

In Table III, a comparison of the experimental results of McFarland and Kinney with those of the present experiment is given in units of angstroms squared. We see that there is almost exactly a factor 2 between the two sets of results. As we have seen, this factor may arise from the ionization detector efficiency in McFarland's experiments and also from the impurities in the neutral beam. Whereas such impurities have not been observed in the beams of other alkali metals, lithium appears to be very difficult to obtain as a pure

TABLE III. Comparison of the results of McFarland and Kinney (Ref. 2) with the present results for the absolute ionization cross section of Li at various energies.

Energy	Absolute ionization cross section ^a	
	McFarland <i>et al.</i>	This work
100	2.2	1.0
200	1.5	0.76
300	1.2	0.57
400	0.99	0.435
500	0.83	0.358

^aIn units of 10^{-16} cm^2 .

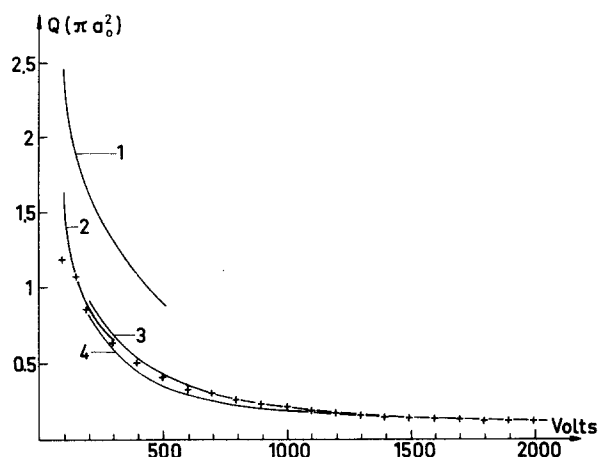


FIG. 10. Absolute ionization cross section of Li by electron impact. 1, McFarland (exp), 2, McDowell (TH), 3, Gaudin (TH), 4, calculated values (this work), +, experiment results (this work).

atomic beam. The presence of impurities in the experiment of McFarland and Kinney seems to be confirmed by the high value of $|Mi|^2$ (about 1) deduced from their results. Also the energy range studied is limited (500 eV maximum) and thus the applicability of the Born approximation questionable. McDowell, discussing the error in McFarland's experiment, estimates an error of $\pm 33\%$. However the difference observed is actually outside the error limits in both experiments. With the present apparatus the total ionization cross section of Mg was also measured and the results are about 15% lower than the results of Kaneko¹⁸ obtained using the same technique. The results were given by this author with an error of $+8\%$ and -23% , and both sets of value are in agreement to within the error limits.

Figure 10 shows a comparison of the experimental results with the calculated results of McDowell¹⁰ (modified Born approximation), of Gaudin and Botter,¹¹ of Omidvar and Sullivan⁸ (Born-Bethe approximation) and, finally with our own results using the treatment given by Gaudin but using the wavefunctions tabulated by Clementi¹⁹ for the target ground state. All the calculated values agree with the present measurements to within the experimental errors.

CONCLUSION

The measurements performed in these experiments may solve one of the problems in the calculations of electron impact ionization cross section at least in the high energy region where the Born approximation is valid. As with the rare gases, the agreement between theory and experiment is very good for Li and for Na, as will be shown in a further publication. More accurate measurements

could perhaps help to solve the problem of which are the best approximations to use in the calculation. However while such measurements are impossible with our present apparatus, they should be possible using the technique developed here for the density measurements of a neutral beam.

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