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Double ionization of rare gases. I. Ion formation by electron impact*

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We have determined the ratio of doubly to singly charged ions for He, Ne, and Ar caused by the impact of electrons with 2 keV energy. Special attention was given to the examination of the reliability of the apparatus with respect to its handling of differently charged ions. The results do not confirm the data of Van der Wiel *et al.*, but they are in good agreement with those of Schram *et al.*

I. INTRODUCTION

The relative cross sections for multiple ionization in rare gases caused by electron or photon impact can yield very sensitive information about the dynamic effect of the electron correlation in atoms. This is because the operator that causes the ionization process is a one-particle operator (for electron impact this is true only in the first Born approximation). Therefore a theory that takes into account neither electron correlation nor rearrangement of the electron orbitals after the ionization process will allow only singly charged ions. Of course, secondary processes, such as the Auger effect, must be excluded by energy considerations. Thus the appearance of differently charged ions, especially doubly charged ions, gives an accurate test for a more refined theory. In the case of photon impact the number of doubly charged ions is a direct criterion for the strength of electron correlation and rearrangement. Such a simple connection is lost in the electron-impact experiment because of the large range of momentum transfer in the collision and possible processes other than ionization in the first Born approximation.

In recent years several experimental investigations for the multiple ionization of rare gases caused by electron[1-9] or photon impact[10-16] have been carried out. For these experiments only the ratio R of doubly charged to singly charged ions shall be considered in the following. The determination of this ratio requires a relative measurement of the cross sections for the differently charged ions. In spite of this important simplification for the experimental technique, the results for this ratio show considerable discrepancies, for electron impact as well as for photon impact. In response to these discrepancies and the importance of correct values which can be compared with theory, a new experiment has been set up with two substantial objectives: (i) no charge discrimination in the apparatus, and (ii) in the photon-impact experiment, a source of photons with well-defined energy. The first phase in our program was the study of the ratio R caused by impact with 2-keV electrons, for He, Ne, and Ar.

II. APPARATUS

In order to avoid charge discrimination in the apparatus, we decided to build a conventional magnetic field mass analyzer with large acceptance, which probably has the least inherent error. A schematic diagram of the apparatus is shown in Fig. 1. An electron gun delivers a well-collimated electron beam with a diameter of about 1 mm.[17] This electron beam traverses the ionization chamber and is trapped in a curved Faraday cup for monitoring the electron current. The inlet of the target gas is a collimated-holes structure which is situated at the bottom of the ionization chamber, 50 mm away from the center. At right angles to the incident electron beam and to the axis of the gas inlet system, the ions produced are extracted out of the electron beam by the weak homogeneous electric field (usually 28 V/cm) of the ionization chamber. This field is applied symmetrically with respect to the center of the chamber, which has ground potential. The ions then enter a stronger homogeneous electric field (usually 138 V/cm) in the acceleration section. At the first plate of this section a thin gold foil with a rectangular opening (10×10 mm^2) is mounted to limit the width of the extracted ion beam in the direction of the incoming electrons. The acceleration voltage is usually kept at -2000 V. Both regions of the electric fields and the end of the acceleration section are separated by an electroformed copper mesh (70 lines/in., 90% optical transmission). After the acceleration section the ions pass into a field-free region with a potential of -2025 V.

In order to handle a fairly large ionization volume with a magnetic field analyzer, an optics system which produces an image with controlled astigmatism is installed in the field-free region.[18]

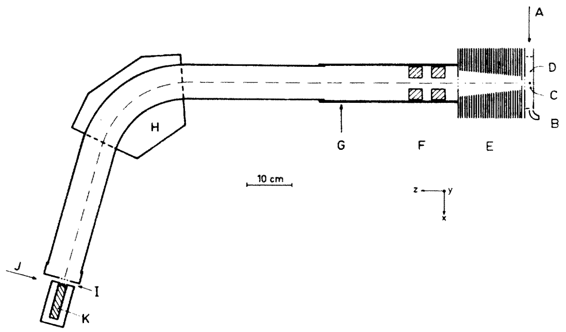

FIG. 1. Schematic diagram of the apparatus. A: electron beam; B: Faraday cup; C: collimated-holes structure; D: ionization chamber; E: acceleration section; F: quadrupole optics; G: focal point of the quadrupole optics; H: 60°-sector magnetic field mass analyzer; I: postacceleration field; J: focal point of the magnetic field mass analyzer; K: Bendix 4700 channeltron.

The optics consists of two electrostatic quadrupole lenses with a field radius $R_0 = 13$ mm, an actual length $L = 30$ mm for the pole pieces, and an actual distance $D = 20$ mm between them. It works in the operation mode where the first lens compresses the beam in the y direction and expands it in the x direction; the second lens then inverts this procedure with a relatively stronger field so that the astigmatic focus is produced. This operation mode gives a focus which is smaller in the y direction compared to the other mode. The focus of the quadrupole optics is placed at the entrance of the 60°-sector magnetic field mass analyzer. In this analyzer ions with a certain e/m are deflected along a curve of 200 mm radius and are refocused at the image. The pole gap of this analyzer is 27 mm, a clearance of 16 mm being left for the ions. In order to reduce the defocusing properties of the fringing fields, the ions enter the pole boundary in the horizontal plane at an angle of 4° (with respect to the perpendicular) and leave the pole boundary at an angle of 11°.[19] The stray field of the magnet at the position of the ionization chamber is smaller than Earth's field. The focus of the magnetic field analyzer is at the entrance of the ion detector, a Bendix 4700 channeltron.

To ensure equal detection efficiencies for the differently charged ions, we require that they have the same velocity before striking the detector.[20] Moreover, good detection efficiencies can be achieved with high velocities. To meet both requirements, the ions are postaccelerated in a strong electric field towards the entrance of the channeltron which is usually at − 7000 V for singly charged ions and − 5000 V for doubly charged ions. Two copper meshes (the same type as above) separate the postacceleration field from the field-free region at the entrance of the channeltron. In order to avoid electron ejection from the edge of the channeltron diaphragm, an additional diaphragm is placed in front of it. It has a slightly smaller opening (5 mm in the x direction, 14 mm in the y direction) and a slightly (1%) more positive potential than the channeltron opening itself. The output pulses of the channeltron are counted by the following equipment: emitter follower, SSRI amplifier (Model 1120, gain 350), ORTEC timing filter amplifier (Model 454, gain usually 20), ORTEC constant fraction discriminator (Model 463, discriminator level usually at 200 mV), fast scaler.

Vacuum is provided by three turbomolecular pumps. The background pressure is better than 5×10^{-7} Torr (6.7×10^{-5} N m^{-2}). When the target gas is introduced, in the region of the source volume one has about 1×10^{-5} Torr (as estimated from known ionization cross sections[21]) and the background pressure rises to about 1×10^{-6} Torr.

III. EXPERIMENTAL CHECKS

The purpose of all experimental checks is the examination of the reliability of the apparatus with respect to its handling of differently charged ions. In brief, the most important items are the following:

(i) Secondary electrons from slits and the Faraday cup would produce predominantly singly charged ions because of their low energies, below 50 eV for most secondaries.[22] Therefore no secondary electrons from beam-defining collimators or from the Faraday cup are allowed to penetrate into the ionization chamber. This was secured by holding the Faraday cup and the other diaphragms (with openings large compared to the electron-beam diameter) at suitable potentials. Above certain values, the counting rates for singly and doubly charged ions did not change as a function of these potentials.

(ii) Because of the initial thermal energy of the atoms and, consequently, of the ions produced, the paths of differently charged ions in the electric fields are not the same. Diaphragms can therefore yield a discrimination by retaining a different amount of the various charge states. In our apparatus all diaphragms have openings large compared to the ion-beam profile, the only exception being the necessary limitation in the direction of the incoming electron beam which is defined by the gold-foil diaphragm. In this direction, the diaphragm accepts slightly different sizes for the source volumes of differently charged

Profile of the Ion Beam at the Focus of the

	Quadrupole Lenses		Magnetic Analyzer
	Out of Action	In Action	
Observed	5 / 12	4 / 2	6 / 2
Estimated	3,8 / 12,0	3,0 / 0,5	6,0 / 1,8

FIG. 2. Profile of the ion beam at different places. The profile was observed with a Bendix 3025 channel plate and connected phosphor screen. The values are given in mm. The accuracy of the observed values is only of the order of 1 mm. For comparison, the ion-beam profile has been estimated by following the path of Ne ions which start in the ionization chamber with a directed thermal velocity perpendicular to the ion extraction field.

ions. In order to have no charge discrimination, it is sufficient that the target gas density be uniform in the slightly different boundary regions of the source volumes. In our case, this condition is fulfilled well because the boundary region is only of the order of 1 mm and the gas inlet is at a distance of 50 mm.

(iii) The profile of the ion beam was observed with a channel plate and a connected phosphor screen (Bendix 3025) and compared with theoretical estimates (for Ne ions with a directed thermal velocity perpendicular to the ion extraction field). Figure 2 shows some typical results. The agreement is good; the largest deviation appears where the ion density per unit area is largest. The observed size of the ion beam (2 mm wide, 6 mm high) at the position of the detector relative to the opening (5 mm wide, 14 mm high) of the diaphragm in front of the channeltron allows three predictions.

First, the counting rate of detected ions as function of the current in the magnetic field mass analyzer must show a plateau because the width of the ion beam is smaller than the widths of the diaphragm opening. A typical example is given in Fig. 3, where the measured counting rate for Ne^+ is compared with the estimated behavior. A change in the magnetic current of $\pm 1\%$ corresponds to a displacement for the ion beam of ± 4 mm, as was observed with the channel plate. The rise and the fall of the counting rate correspond to the width of the ion beam, and the full width at half-maximum corresponds to the width of the diaphragm opening. The small variation of the counting rate in the region of the plateau is due to some surface sensibility of the channeltron.

Second, the height of the ion beam is smaller than that of the diaphragm opening in front of the channeltron. This allows—within certain limits—a shift of the height of the ion beam without any

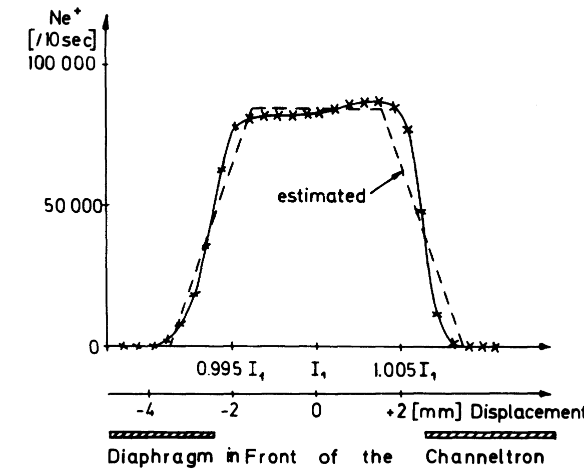

FIG. 3. Counting rate for Ne^+ ions (crosses) as a function of the current I_1 in the magnetic field mass analyzer ($I_1 = 1.115$ Å) or as function of the displacement of the ion beam at the position of the channeltron. For comparison, the estimated behavior is also shown. In this measurement a new channeltron (II) has been used. The Ne pressure was about 1.3×10^{-5} Torr in the region of the source volume and the electron current was 2.5×10^{-10} A.

change of its transmission. This means that the electron beam may cross the ionization chamber at different heights without any change of the transmission for the ions. These height limits for the dimension of the source volume were found to be ± 2.5 mm with respect to the center.

Third, the observation and the check of the ion-beam profile with the channel plate yields also

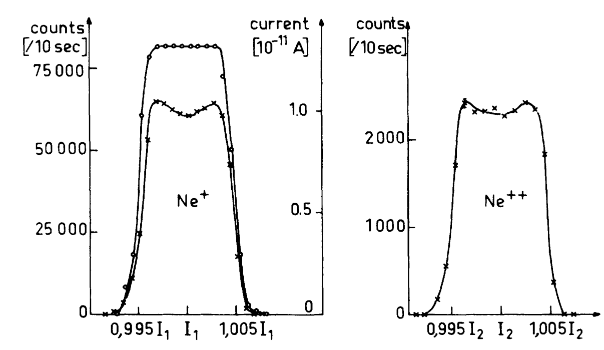

FIG. 4. Ne^+ and Ne^{++} counting rates (crosses) as registered by channeltron I and Ne^+ current (circles) as measured in a Faraday cup instead of the channeltron. These quantities are shown as function of the current in the magnetic field mass analyzer ($I_1 = 1.115$ A and $I_2 = 0.773$ A). In these measurements, the diaphragm opening in front of the channeltron was only 4 mm wide instead of the 5 mm used later. The Ne pressure was about 1.3×10^{-5} Torr in the region of the source volume and the electron current was 2.5×10^{-10} A for the counting and 2.5×10^{-6} A for the current measurement, respectively.

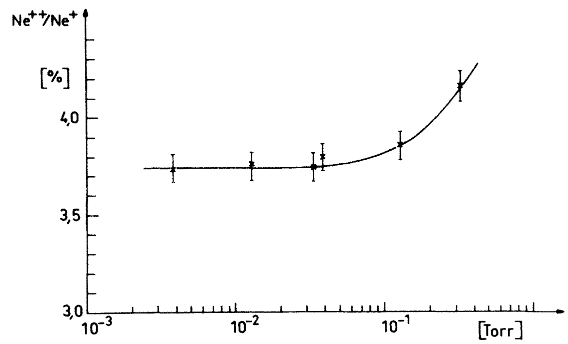

FIG. 5. Ratio Ne^{++}/Ne^{+} as a function of the pressure measured at the high-pressure side of the collimated-holes structure. A value of 5×10^{-2} Torr corresponds to about 2×10^{-5} Torr in the region of the source volume.

the information that—apart from losses at the copper meshes—one can rely upon a 100% transmission of the ions up to the focal point of the quadrupole optics and even up to the entrance of the channeltron. Since the fringing field of the magnetic field mass analyzer is very critical for the ion path, the transmission through the analyzer has been proved by a measurement of the ion current with a Faraday cup at the input of the analyzer and at the place of the channeltron. This measurement confirmed the 100% transmission through the magnetic field mass analyzer.

(iv) Even for ions with the same velocity, the absolute detection probability may depend on the condition (pollution) of the channeltron surface and on the point of ion impact on the channeltron (surface sensibility). A typical example is shown in Fig. 4, where the ion beam was made to hit different parts of the channeltron surface by changing the current in the magnetic field mass analyzer. With respect to the measurement of the ion current with a Faraday cup, the deviating features for the counting properties of the channeltron can be seen clearly: no flat plateau and a reduced detection efficiency [in this example, about 77% for a 1-yr-old channeltron (channeltron I) which no longer had a peaked pulse-height distribution; a new channeltron (channeltron II) gave 100%]. Further measurements of this kind have shown that peak shape and reduced detection efficiency have no influence on the ratio R, provided the whole peak is scanned in each case and equal parts of the plateau are used for the evaluation of the data.

(v) The relation between the observed counting rate and the current of the electron beam was linear up to 10^4 counts/sec and independent of the absolute detection probability of the channeltron.

(vi) A possible charge discrimination may occur owing to some charge transfer on a copper mesh. With an additional displaceable mesh behind the acceleration section, the ratio R was tested and found to be constant within the experimental error of 0.5%. The influence of the mesh at the ionization chamber on the ions with lower velocity could not be checked, but it should be small because of the above result.

(vii) To be sure that ion-molecule reactions do not influence the results, the pressure dependence of the ratio R was examined for He, Ne, and Ar. Figure 5 gives an example. The ratio R is shown as function of the pressure measured at the high-pressure side of the collimated-holes structure. Because of the relatively weak differential pumping between the ionization chamber and the rest of the apparatus, a higher pressure of the target gas results also in a rise of the background gas pressure. The change of R as given in Fig. 5 is then the result of pressure-dependent processes inside and outside of the ion source. Assuming that each interaction of an ion with a neutral particle will prevent the detection of this ion, the number of transmitted ions is reduced by a factor of $1-\alpha$, where α may be different for singly or doubly charged ions and is dependent on the pressure. An unpronounced pressure dependence of the ratio R then indicates that possible pressure effects are small or not strongly charge dependent. Only those data with negligible pressure effect have been used.

(viii) The ratio R has been determined with conditions for the electric fields that were different

TABLE I. Ratios R of doubly charged to singly charged ions caused by impact of 2-keV electrons. Values are given in percent and relative to the intensity of single ionization processes. Errors in the last decimal place are given in parentheses.

Ion	Researcher	Reference	R
He^{++}/He^{+}	Schram *et al.*	2	0.42
	Gaudin and Hagemann	5	0.55
	Van der Wiel *et al.*	6	0.58
	This work		0.42(8)
Ne^{++}/Ne^{+}	Ziesel	1	4.4
	Schram *et al.*	2	3.4
	Adamczyk *et al.*	4	4.1
	Gaudin and Hagemann	5	4.4
	Van der Wiel *et al.*	6	6.0
	This work		3.7(3)
Ar^{++}/Ar^{+}	Schram	3	5.3
	Gaudin and Hagemann	5	5.7
	Van der Wiel *et al.*	6	8.8
	This work		5.0(4)

from those given in the description of the apparatus. It was found that the ratio R is constant (a) within an experimental error of $\pm 1\%$ when the extraction field in the ionization chamber is changed from 10 to 35 V/cm, (b) within $\pm 0.5\%$ when the acceleration voltage is changed from -2000 to -2500 V, and (c) within $\pm 1.5\%$ when the postacceleration voltage towards the entrance of the channeltron is varied between -5 and -10 kV and between -3.5 and -7 kV for singly and doubly charged ions, respectively.

IV. RESULTS AND DISCUSSION

Table I gives a compilation of our ratios R for He, Ne, and Ar caused by the impact of electrons with 2 keV energy, together with the results of other authors. The most important checks listed above, together with further investigations under conditions different from those described (in particular, different regions of the source volume, new channeltrons, total readjustment of the entire setup), have demonstrated that an inherent error of about 7% should be ascribed to our results. In the case of He, an additional error of about 12% occurs because of the low counting rate of He^{++} and the amount of the H_2^+ peak whose main part coincides with the main parts of He^{++}. The compilation shows that our data deviate from those of Van der Wiel *et al.*[6] On the other hand, our results are consistent with those of Gaudin and Hagemann,[5] which have probably an error of[23] 20%, and with the value of Ziesel.[1] They also agree very well with those of Schram and coworkers[2-4] which have an error of 5–10%.

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