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SINGLE AND MULTIPLE IONIZATION OF LEAD ATOMS BY ELECTRONS

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An analysis is carried out of methods of measuring true cross sections for ion production by electron impact. To measure true cross sections one must know exact values for the proportionality constant between the ion current in the source and the ion current recorded by the detector or else apply the so-called difference method. We use the difference method to measure cross sections for electron impact production of the ions Pb^+ to Pb^{5+}. The cross sections are normalized according to the known value of the total cross section. The measured cross section for single ionization of lead at energies above 260 eV agrees with that calculated in the Born approximation. Structure can be discerned in the initial part of the single ionization curve. The results confirm the power threshold law for single and double ionization of lead atoms by electrons.

INTRODUCTION

THE study of single ionization of atoms on collision with electrons enables us to compare the probabilities of various transitions in the atom under equivalent conditions of excitation and to obtain additional information about the properties of the electron cloud.

The first results on the measurement of the probability of formation of multiply-charged ions of mercury and certain gases were obtained in 1930 by Bleakney[1] who used crossed magnetic and electric fields to separate the ions. An analyzer of such a type has a low resolution and therefore the accuracy of the measurement is not great. Subsequently Bleakney used a Dempster-type analyzer with a deflection through 180° in a homogeneous magnetic field.[2] A similar arrangement was used in the experiments of Tate and Smith.[3]

In the 1960's, after a long interval, experiments in the study of multiple ionization were begun. Brink investigated certain alkali metals,[4] and Crawford and Wang measured cross sections for single and double ionization of silver.[5] In these experiments a quadrupole mass spectrometer was used to separate the ions. Apart from this, a series of works was carried out using magnetic mass spectrometers, with either a standard or modified ion source;[6-8] in most of this work, however, consideration was given not to the determination of the absolute value of the cross section, i.e., of the true cross section, but to the investigation of the relative variation of the ionization functions. As regards absolute measurements, Kieffer and Dunn in their survey[9] cite data on only ten elements (He, Ne, Na, Ar, K, Kr, Rb, Xe, Cs and Hg).

In the present work an analysis is given of methods for obtaining absolute values of cross sections for production of ions of known charge, along with experimental results for the determination of ionization cross sections of lead atoms.

1. METHODS FOR MEASURING TRUE IONIZATION CROSS SECTIONS

All methods for determining the true electron impact ionization cross section are based on the measurement, in single-collision conditions, on the quantity N_{in} of positive ions of definite charge $q/M = ne/M$ produced for known energy E and quantity N_e of the bombarding electrons, when the concentration of neutral atoms is n_a and the path length in which the ions are detected is l. These quantities are connected by the relation $N_{in} = N_e n_a \sigma_n l$, where σ_n is the cross section of the n-tuple ionization and $n = q/e$ is the charge of the ion in units of the electron charge.

In an ideal experiment it is necessary to effect a complete separation of all the ions by their charge-mass ratio using a mass spectrometer. In practice it is not possible to guarantee 100% detection of the ions. As a rule only part of the ions are extracted from the ionization chamber and, besides this, a certain fraction of the ions are lost in the analyzer.

Generally the current recorded by the detector differs from the current of the corresponding ions in the source:

$$[I_{in}(E)]_{\text{det}} = k_n [I_{in}(E)]_{\text{sou}}. \qquad (1)$$

Here k_n is a proportionality constant characterizing the ion source, analyzer and detector; k_n may depend on the electron energy $E = eU_e$, on the electron current I_e, on the charge-mass ratio q/M of the ion, on the initial energy of the ions in the source, on the concentration of neutral particles and on the properties of the detector. In performing the measurements in practice, a linear dependence of ion current on electron current and on the concentration of the substance investigated is always obtained and therefore we shall not take account of the influence of these factors on k_n. To obtain reliable absolute measurements it is necessary to take the sensitivity of the ion detector into account. There remain two sources of discrimination: 1) change of k_n with change of electron energy: $k_n = f(E)$, 2) the dependence of k_n on the nature of the ion: $k_n = f(q/M)$. The latter includes the effect of the initial ion velocities if this is due to some distinctive feature in the ion formation, e.g., the result of dissociation of a molecular ion. Indeed, the energy spectrum of ions in this case is uniquely determined by the nature of the initial molecule and of the ion formed.

We shall consider certain particular cases. If k_n

depends on E and does not depend on the nature of the ion, then at fixed energy the ratio of the ion currents at the analyzer exit will be the same as at the source, i.e.,

$$\left(\frac{I_{in}}{I_{i1}}\right)_{\text{det}} = \left(\frac{I_{in}}{I_{i1}}\right)_{\text{sou}} = c_n. \tag{2}$$

Therefore, knowing the total ionization cross section σ_{tot}, one can determine the true cross section for n-tuple ionization:

$$\sigma_n = \sigma_{\text{tot}}\, c_n / (1 + c_2 + c_3 + \ldots). \tag{3}$$

This method is used by the majority of researchers in spite of the absence of a rigorous proof that k_n does not depend on q/M. What is more, in the experiments[1-4] analysis of the ions is effected, at constant magnetic field, by variation of the electric field, not in the whole but in part of the instrument; consequently, the scaling law is violated and ions of various charges move along different trajectories. In the work,[8] analysis of the ions is effected by change of the analyzer magnetic field, whereas in the ion source there is no magnetic field. Thus the scaling law is satisfied and from the standpoint of electron optics there must be no discrimination. Such a method must be assumed to be reliable, although use of an electron source with electrostatic focussing makes the work difficult in the low energy range and also complicates the measurement of the total ion current.

The use of an electron source with a collimating magnetic field has a number of advantages: it guarantees a constant beam shape and constant dimensions of the ionization region, enables one to work with low energy beams, facilitates the separation of the ion current from the electron current, etc. However, in a magnetic field, ions with different charges move along different trajectories and this can lead to violation of the relation (2). In this case another method for obtaining true ionization cross sections can be proposed, the so-called difference method, which is applicable when k_n does not depend on the electron energy E but depends only on the nature of the ion. In this the dependence on electron energy of the ion current at the detector and the source are similar and differ only in scale, whilst the currents for different ions are not the same. In the difference method the total ionization cross section and the relative cross sections for production of ions of known charge are measured as a function of electron energy. Then a systematic calibration of the multiple ionization curves is performed with respect to the total ionization cross section. The error in the calibration by the difference method depends on the amount of scatter in the experimental curves for the total and partial cross sections and increases with decrease of the partial cross sections.

We must refer to another special case, when $k_n = 1$. It is possible, for example, to obtain such a condition by means of ion analysis in crossed fields with cycloidal motion of the ions;[10, 11] however, in practice this method is almost never applied in measuring true cross sections.

DESCRIPTION OF THE INSTRUMENT AND OF THE EXPERIMENTAL METHOD

The instrument for measuring the true ionization cross sections of lead consists of an atomic beam source, an electron source and an ion analyzer, all placed in a metal-glass tube.

The atomic beam was produced by evaporation of the investigated substance from a molybdenum crucible with a tungsten heater; four slits were used to shape the beam. The instrument was fitted with a shutter for modulation of the atomic beam.

A gun of the tetrode type[12] with an end-window oxide cathode and a collimating homogeneous magnetic field was used as the electron source. The power supply of the source was from BAS-80 dry batteries.

Application of the difference method presupposes the measurement in one experiment of the dependence on electron energy of the total ion current and of the currents of ions of different charges. It was possible either to collect the ions formed in the ionization chamber at the collector for the total ion current or to direct them into the entrance of the mass analyzer. To focus the ions into the entrance of the analyzer, a system of cylindrical lenses, analogous to that described in [13], was used. This system makes it possible to compensate the deflection of the ion beam in the collimating magnetic field. A single-pole mass filter[14] has been selected as the ion analyzer, since it has a number of favorable properties: the scheme and construction are simple and the sensitivity and resolution are, within broad limits, independent of the energy and angle of incidence of the ions and of the pressure of the residual gas.

To amplify the ion current after passage through the analyzer, a ten-stage electron multiplier with copper-beryllium emitters was used. The modulated total ion current or the current from the electron multiplier was measured by a U1-2 electrometer amplifier, the output of which was connected to an S1-4 oscilloscope. Provision was made for tracing the ionization curves on a two-coordinate N-359 automatic recorder. In this case the curve was recorded twice on one graph, with the shutter of the atomic beam modulator open and closed.

The principal elements of the experimental apparatus are shown schematically in Fig. 1. The apparatus was evacuated with a TsVL 100 oil pump with nitrogen traps. After annealing at a temperature of 300–350°C for 24 hours, the residual gas pressure at room temperature was reduced to 2×10^{-7} mm Hg. Before the measurements, a check was made of the completeness of the drawing off of the ion to the total-current collector and of the linearity of the dependence of the ion current on the electron current; in this way the operating conditions of the electron source were determined, i.e , the range of variation of the electron current and the ion extraction voltage.

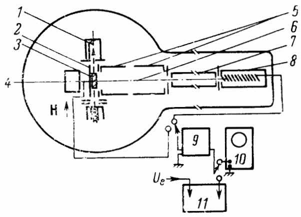

FIG. 1. The experimental setup for measuring single and multiple ionization of atoms by electron impact: 1 – electron beam, 2 – total ion current collector, 3 – atomic beam, 4 – atomic beam shutter, 5 – ion lenses, 6 – ion beam, 7 – single-pole mass filter, 8 – ten-stage electron multiplier, 9 – electrometer amplifer, 10 – oscillograph, 11 – two-coordinate automatic recorder.

After the measurement of the dependence of the total current on the electron energy, the ion flux was diverted into the analyzer, which was adjusted for ions of different mass; analogous curves were plotted for these ions. The ion-focussing system was adjusted for different energies of the source electrons. The agreement of the final results gives us reason to assume that in the conditions of the experiment k_n does not depend on the energy of the electrons. The good applicability of the difference method serves as further confirmation that k_n is independent of energy. The difference $I_{tot} - I_{i1}$, within the limits of the scatter of the experimental points, is directly proportional to I_{i2} in the energy range from eU_{i2} to eU_{i3}; the difference $I_{tot} - I_{i1} - I_{i2}$ is proportional to I_{i3} in the range of energies from eU_{i3} to eU_{i4}, and so on.

In the instrument described, no provision was made for measuring the concentration of neutral particles and, therefore, the known absolute value of the total or apparent ionization cross section[12] was used for the calibration.

3. RESULTS OF THE MEASUREMENTS

Lead was selected for the measurements, since we had earlier measured the absolute value of its total ionization cross section[12] and had carried out a calculation of the single-ionization cross section of lead in the Born approximation.[15] The ion current curves for Pb^+ to Pb^{5+} were measured in the range of ionizing electron energies from the threshold to 400 eV and the total ion current was measured in the range 7.5 to 200 eV. The averaged curves were plotted on the basis of five to seven experimental curves.

The coefficients k_n, determining the contribution to the total current of ions of charge ne, were successively determined from the relations

$$I_{i1} = k_1 I_{\text{tot}} \quad \text{for} \quad eU = eU_{i1} - eU_{i2},$$
$$I_{i2} = k_2 (I_{\text{tot}} - I_{i1} / k_1) \quad \text{for} \quad eU = eU_{i2} - eU_{i3},$$
$$I_{i3} = k_3 (I_{\text{tot}} - I_{i1} / k_1 - I_{i2} / k_2) \quad \text{for} \quad eU = eU_{i3} - eU_{i4}.$$

This method gives unreliable results for the Pb^{4+} and Pb^{5+} ions and so another method of evaluation was used for these, namely extrapolation of the curve of k_n against the charge-mass ratio q/M of the ion.

To obtain the absolute values of the cross sections the ion current curve was normalized at its maximum using the known ionization cross section of lead.[12] The total ionization cross section of lead and the cross sections for single and multiple ionizations are shown in Fig. 2. The coordinates of the latter are multiplied by the charge multiplicity of the ion and thus correspond in scale to the corresponding ion currents. The cross section values at the maximum and the energies corresponding to them are shown in the table. The root mean square error of the measurement is also given there. In Fig. 3 the ionization curves for Pb^{3+}, Pb^{4+}, and Pb^{5+}, reduced to unity at the maximum, are drawn on a larger scale.

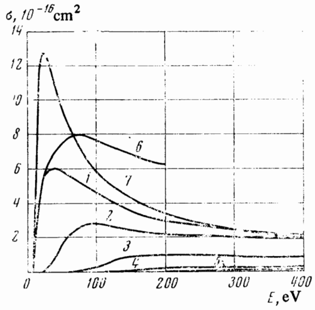

FIG. 2

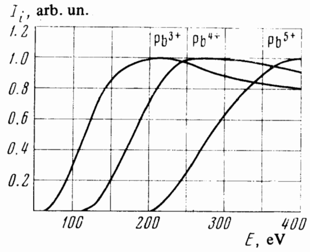

FIG. 3

FIG. 2. Electron impact ionization cross sections of lead atoms: curve 1 – σ_+, 2 – $2\sigma_{2+}$, 3 – $3\sigma_{3+}$, 4 – $4\sigma_{4+}$, 5 – $5\sigma_{5+}$, 6 – $\sigma_{tot} = \sum_{n=1}^{5} n\sigma_{n+}$, 7 – Born approximation estimate.

FIG. 3. Ionization curves, reduced to unit at the maximum.

	σ_{max}, 10^{-16} cm²	E_{max}, eV	Root mean square error, %		
			Scatter in the curves	determination of k_n	
				experiment	theory
σ apparent	8.0	75	0.8	—	—
σ_+	6.03	40	1.6	0.4	1.5
σ_{2+}	1,4	100	2,7	1,2	4,1
σ_{3+}	0.32	210–220	0.9	2.6	17
σ_{4+}	0.056	260	1	—	106
σ_{5+}	0.0106 (at 400eV)	>400	—	—	—

Note: here σ_{max} is the greatest value of the cross section and E_{max} is the energy corresponding to it.

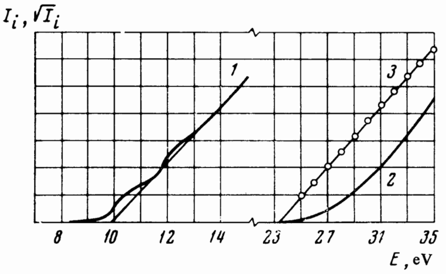

FIG. 4. Variation of the ionization curves near the threshold (the energy is uncorrected and the current is in relative units): 1 – single ionization, I_{i1}, 2 – double ionization, I_{i2}, 3 – $\sqrt{I_{i2}}$.

In Fig. 2 the measured single ionization cross section of lead (curve 1) and the cross section calculated in the Born approximation (curve 7) are shown for comparison. The results of the calculation were previously compared[15] with the total ionization cross section. From Fig. 2 it is clear that at energies above 260 eV the experimental and calculated values coincide.

In Fig. 4 the variation of the initial parts of the curves is shown for (1) single and (2) double ionizations, recorded using the automatic recorder. The results confirm the presence of structure, observed in the work,[15] in the single-ionization curve of lead. To check the threshold law for the cross section of the double ionization, a curve of the square root of the ion current against energy was plotted. This dependence (Fig. 4, curve 3) is linear, which is evidence that the power law $\sigma_{2+} \propto (E - eU_{i2})$ is correct.

CONCLUSION

The analysis of methods of studying true ionization cross sections shows that the methods of checking the absence of ion discrimination in the analyzer are inadequate. The difference method for calibrating the relative cross sections against the absolute value of the total cross section does not require account to be taken of discrimination in the analyzer and possesses definite advantages. The difference method guarantees adequate accuracy for those cross sections which are not too small compared with the total ionization cross section.

The measurements carried out for the ionization cross section of lead demonstrated the possibility of applying the method to determining cross sections for the ions Pb^+ to Pb^{3+}. The production cross sections of Pb^{4+} and Pb^{5+} were estimated. In the range from the threshold to 400 eV the ion currents I_{in} for each energy are greater than the currents I_m, where $m > n$. A study of the threshold behavior of the ionization cross sections confirmed the presence of structure in the curve for single ionization and the quadratic character of the variation of cross section for double ionization.

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