

ABSOLUTE VALUES OF ELECTRON IMPACT IONIZATION CROSS SECTIONS FOR
MAGNESIUM, CALCIUM, STRONTIUM AND BARIUM

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Absolute values of electron impact ionization cross sections for alkali-earth metal vapors are measured within the ionizing electron energy range from threshold to 200 eV. The precision of measuring the absolute ionization cross section values is improved in comparison to previously published data and reaches 17% due to increased sensitivity of the ionic current meter and the use of a new method of measuring the concentration of neutral atoms in the atomic beam. Increasing atomic weight is accompanied by increasing absolute values of ionization cross sections and the appearance of two peaks. Theoretical computations performed in Born and classical binary approximations are in good agreement with experimental results.

MEASUREMENTS of ionization cross sections based on a simple gas-kinetic relation

$$\sigma = I_i / I_e n_a L \quad (1)$$

(where I_i and I_e are ionic and electronic currents, n_a is atomic concentration in the collision region, and L is the interaction length) have been performed since the Twenties; however the majority of the published papers deals with gases and among the fairly large number of papers on ionization cross sections of metals that are known to us only 21 papers report independent absolute measurements of apparent ionization cross sections of metal atoms by electron impact from the ground state^[1].

Analysis of these papers shows that the most precise and promising is the method of crossed modulated beams, which provides for a reliable measurement of concentration of neutral atoms. It is the direct measurement of neutral atom concentration in the beam that has been the obstacle that prevented to this day the development of a reliable method of measuring apparent electron impact ionization cross sections of metals.

1. MEASUREMENT OF THE CONCENTRATION OF NEUTRAL PARTICLES IN ATOMIC BEAMS

Although a large number of various methods of measuring low concentration of neutral particles in beams is known^[2], only two methods found a sufficiently wide acceptance in experiments measuring ionization cross section of substances with a low vapor pressure. These are the method of surface ionization and the method of condensation target^[1]. The first method consists in ionization of atoms on the surface of a heated tungsten wire taking advantage of the fact that the electron work function for tungsten is higher than the ionization potential of the investigated substance. The obtained ions are gathered by the collector and their current is measured by an electrometer. Three processes take place simultaneously in this case: atoms are condensed on the surface of a hot tungsten wire, atoms are ionized on this surface, and ions are

vaporized from the surface. Each process can be characterized by corresponding coefficients α_1 , α_2 , and α_3 , which were usually assumed equal to unity by all investigators^[3-6]. This, however, may not be always true.

McFarland used the following experimental procedure in an attempt to bring the ionization coefficient α_2 on the surface of a hot tungsten filament close to unity. At the filament temperature $T = 1300^\circ\text{K}$, oxygen was admitted to the system at a pressure 10^{-6} Torr to increase the work function. However, the ion vaporization coefficient α_3 was much lower than unity at this temperature, and furthermore at this temperature alkali metals condensed on the tungsten surface, decreasing the work function. Therefore after oxidation at $T = 1300^\circ\text{K}$ the filament temperature quickly rose to $T = 2230^\circ\text{K}$ and a current of ions generated by surface ionization was observed for some time in spite of the fact that at this temperature the oxide film on the tungsten surface is destroyed and the work function actually decreases continuously. Because of this filament oxidation had to be repeated many times during a single experiment with the result that all three coefficients α_1 , α_2 , and α_3 , which determine the ion current due to surface ionization, varied during the measurements and it was not possible to take this variation into account.

Being aware of this, McFarland attempted a special analysis of the ionization coefficient α_2 . The analysis showed, according to^[7], that this coefficient is close to the expected values only for Li and Na, whereas for all other metals the obtained values of ionization cross sections are merely order-of-magnitude estimates^[1]. Because of the experimental complexity, McFarland could determine ionization cross sections of each metal only at six points corresponding to electron energies of 500, 400, 300, 200, 100, and 50 eV.

Zapesochnyi and Aleksakhin^[8] used a variant of the condensation-target method. The condensate mass was determined from the frequency "drift" of a quartz vibrator serving as the condensation target of the atomic beam. The chief disadvantage of this method

(as of all other variants of the condensation method) is the unknown value of the alkali-metal condensation coefficient for a quartz plate, which the authors had to assume equal to unity.

We used several variants of the condensation method to determine the concentration of atoms in the beam: the condensate mass was determined by the tagged atom method^[9] or by the gravimetric method^[10,11]. The condensation coefficients for silver and copper were taken from Knudsen's measurements^[12] and from^[13], while the condensation coefficient for lead was determined from our own experiments^[14].

2. EXPERIMENTAL METHOD

In work with Group II metals, whose condensation coefficients are unknown, the concentration of neutral atoms in the beam was determined with the aid of atom trap 8 (see Fig. 1) representing a condensation target in the form of a hollow double cylinder with a narrow entrance slot. Relative to the atomic beam such a trap is a "black body" whose degree of blackness, determined from geometric considerations taking both specular and diffusive reflection into account, amounts to over 98%. The condensate was washed off the internal surface of the trap and its mass was determined by the atomic absorption method with an accuracy of 4–5%. This method eliminated the need to determine the condensation coefficient. Furthermore we could measure the condensation coefficients of the investigated metals by measuring separately the condensate mass deposited on the bottom of the trap and on the remaining internal surface. Under our experimental conditions, for glass and liquid nitrogen temperature, they were found to be: 0.66 for Mg, 0.75 for Ca, 0.77 for Sr, and 0.81 for Ba. The accuracy of measurement of condensation coefficients was 8–10%.

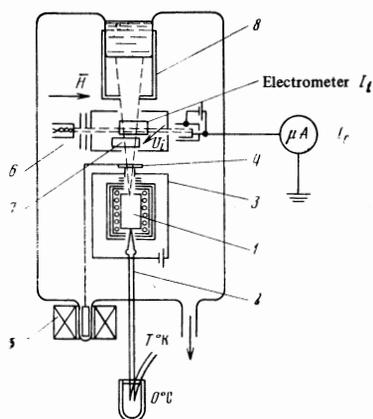


FIG. 1. Diagram of the experimental setup.

The concentration of the atoms in the beam was computed from the formula

$$n_a = M_c / mbLvt, \quad (2)$$

where M_c is the condensate mass, m is the atomic mass (in g), bL is the cross sectional area of the collision region (in cm^2), t is the total deposition time (in sec), and $v = 1.33 \sqrt{2kT/m}$ is the mean thermal velocity of atoms (in cm/sec).

It follows from (2) that the method of computing n_a yields an integral result so that in the experiment considerable care was required to maintain the stability of parameters of the atomic beam during the entire procedure. Heated diffusion chamber 1 in a multilayered shield served as the atomic beam source. The diffusion chamber temperature was measured with platinum-platinum-rhodium thermocouple 2 in the coldest zone of the chamber. The temperature distribution along the length of the diffusion chamber was determined under operating conditions. The working temperature of the vapor was selected so as to have the mean free path of atoms in the collision region longer than the reactor vessel length to assure a molecular regime of the atomic beam. The molecular nature of the beam could be monitored by observing the sharp boundary between the shadow and half-shadow at the condensate film. The atomic beam was shaped by a system of diaphragms, purged of thermal ions drawn to plates 3, and interrupted by shutter 4 with a period of 8 sec. The shutter drive was represented by two-section magnet 5. The temperature of the diffusion chamber was gradually increased with the shutter closed while the metal charge was outgassed. A vacuum of at least 3×10^{-6} Torr was maintained in the apparatus during the entire experiment. Standard electron tetrode gun 6 with indirectly heated oxide cathode generated an electron beam current of $1-2 \mu\text{A}$. A constant uniform magnetic field $H = 150$ Gauss was coaxial with the electron optical system to focus and stabilize the beam. The electron energy could be varied up to 200 eV. An electron collector in the form of a Faraday cylinder with a central positive electrode ensured a complete capture of electrons. The completeness of electron capture was monitored by observing the saturation of the current-voltage function at the central electrode of the Faraday cylinder. The fraction of electrons in the beam due to ionization did not exceed $10^{-2}\%$. The ions obtained in the collision region were drawn to plates 7 by the field U_i whose magnitude for various electron energies was determined from the saturation of curves representing ion current as a function of the drawing field.

The ac component of the ion current was delivered to the electrometer through a vacuum seal terminal with a resistance to ground $> 10^{14}$ ohms. The electrometer readings were converted by a digital voltmeter and printed out. This method was also used to measure the electron energy. This simple mechanization of the measurement procedure significantly enhanced the reliability of the obtained data merely because it permitted a sharp increase in the number of measurements.

In these experiments collisions occur in a magnetic field that can impart a specific orientation to atoms in the beam whenever atoms possess a magnetic moment. This was first pointed out to us by V. A. Fabrikant. In the case of Group II metal atoms whose magnetic moment is zero this phenomenon is negligible. The method did not provide for a special determination of vapor composition. We assumed it to be monatomic for Group II metals according to data in^[15,16].

Taking the two last remarks into account we can conclude that our method makes it possible to measure

in a single experiment all quantities that are necessary to obtain the numerical value of metal ionization cross sections, a necessary condition for absolute measurements.

3. DISCUSSION OF RESULTS

Figure 2 shows the obtained results of measuring absolute values of ionization cross sections for Mg, Ca, Sr, and Ba.

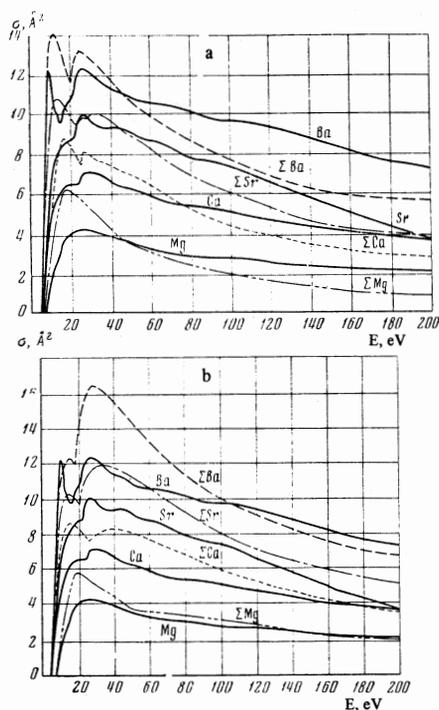


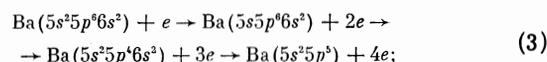
FIG. 2. Absolute values of electron impact ionization cross sections for alkali earth metals. a—comparison of experimental results (solid lines) with computed values obtained from Born approximation; b—comparison of experimental results (solid lines) with computed values obtained from the binary approximation of classical mechanics; Σ is total computed cross section.

We can consider two types of errors in the given curves. The error in measurement of the relative value of ionization cross sections amounts to 9%; this is an error in measuring two currents, ionic and electronic. The total relative error is considered. In all experiments the beam electrons were monoenergetic within 0.35 eV; this was verified earlier with the aid of electrostatic and magnetic electron selectors^[11]. Each curve in Fig. 2 is an average of 12–20 measurements carried out at different times, with different instruments, and under different experimental conditions. The error in the measurement of absolute values of ionization cross sections amounts to 16–17%. The scatter of curves did not exceed 8%.

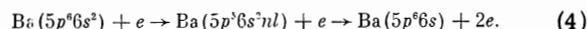
Comparison of the obtained results shows that the curves are on the whole similar. The principal peaks of all the curves are located in the region of 26 eV. At the same time, moving within the subgroup from Mg to Ba, we discover a tendency towards increasing the absolute cross section value in the curve maximum from 4.2 Å² for Mg to 12.5 Å² for Ba. The slope running

to the peak increases and there is a clear tendency to form two peaks. The most interesting are two clear peaks in the Ba ionization cross section curve observed for the first time. All curves have some breaks and bends in the down slope beyond the peak. Most of these coincide fairly accurately with the potentials of the corresponding multicharged ions. We can readily assume that the second peaks in the Ca, Sr, and Ba ionization cross section curves are due to the appearance of doubly charged ions. To verify this we made a number of ionization cross section computations for the given elements.

Ionization in a multielectron atom can be due to the following processes: (a) ionization directly from the outer shell; (b) ionization from inner shells. The latter process is usually accompanied by autoionization emission of one or several additional electrons. For example,



(c) excitation of an electron from an inner shell with subsequent autoionization. For example,



Some other mechanisms were also possible (such as a direct multiple ionization) but were not considered in our computations. We also note that only electrons from a few outer shells participate in the autoionization transitions mentioned in (b) and (c) since the contribution from deeper shells is too small. For these electrons the effective nuclear charge is comparatively small and thus the emission probability can be fully neglected and Oje transitions can be assumed to have 100% probability.

Ionization functions were computed in Born approximation and in binary approximation of classical mechanics. Born computations were performed according to a universal program that computed both the cross sections and the necessary wave functions for the continuous and discrete spectra. The methodology of these computations was described earlier^[17].

Classical computation was performed according to formulas representing a modification of Stabler's formulas^[18]. The modification consists in considering the acceleration of the incident electron by the field of the neutral atom. This effect was apparently first considered by Thomas, Vriens, Burgess, and Percival^[19–22]; however as far as we know the acceleration effect was not given sufficient attention in actual computation. Incidentally it is far from small: in the peak region it decreases the cross section approximately by a factor of two. Furthermore it seems to us that the formulas and assumptions underlying the classical binary approximation cannot be considered self consistent without taking this effect into account. The methodology of the classical computation is therefore treated in greater detail.

In the binary approximation only the electron-electron interaction is usually considered and electron interaction with the nucleus is neglected. It follows directly that this approach is valid only if the distance between electrons r_{12} is small relative to their distances r_1 and r_2 from the nucleus. Consequently

Stabler's formulas as well as analogous formulas of other authors correctly describe the collision dynamics only in some sufficiently small region and not in the entire space. Stabler showed that the differential cross section $d\sigma/d\epsilon$ for the transfer of energy from a free electron with pre-collision velocity v to an atomic electron with a velocity v_a is

$$\frac{d\sigma}{d\epsilon} = \frac{1}{v} \frac{\pi e^4}{e^2} \left(\frac{2E_{min}}{mEE_a} \right)^{1/2} \left[1 + \frac{4}{3} \frac{E_{min}}{|e|} \right] \quad (5)$$

where E and E_a (E' and E'_a) are kinetic energies of the first and second electrons before (and after) collision, and E_{min} is the smallest of these four numbers. Stabler's formulas are most applicable to the case of a fast electron colliding with an atom when the main electron energy transfer necessary for ionization actually occurs at interelectron distances that are small relative to the dimensions of the atom. This case makes particularly clear the fact that (5) implies electron velocities at the entrance to the electron pair interaction region rather than those far away from the atom. The interaction itself takes place at the same distance r_a from the nucleus as that of the atomic electron.

We see thus that in formulas derived without taking the nuclear interaction into account the kinetic energy E of the incident electron should be replaced by $E + V(r_a)$, where $V(r_a)$ is the potential energy of the electron in the atom. We assume here that $V(r_a) = 2E_a = 2I$ which is true of hydrogen and helium atoms and remains sufficiently valid for the other cases. I denotes the ionization potential. Such a substitution however always makes E_a the lowest energy of the four, E , E_a , E' , and E'_a , and (5) converts into

$$\frac{d\sigma}{d\epsilon} = \frac{\pi e^4}{E + 2I} \frac{1}{e^2} \left[1 + \frac{4}{3} \frac{I}{|e|} \right], \quad (6)$$

For the total cross section we obtain

$$\sigma^{ion} = \int \frac{d\sigma}{d\epsilon} d\epsilon = \pi a_0^2 (Ry^2/I^2) f(x), \quad (7)$$

$$f(x) = \frac{4}{3} \frac{x-1}{x(x+2)} \left(5 + \frac{2}{x} \right). \quad (8)$$

A generalization to the case of a multi-electron atom obviously yields

$$\sigma^{ion} = \pi a_0^2 Ry^2 \frac{n_i}{I_i^2} f(x_i). \quad (9)$$

Here a_0 is the Bohr radius, I_i is the ionization potential of the i th shell, $x_i = E/I_i$, and Ry is the Rydberg constant. These formulas were used in the computations involving the first five shells.

The energy values of internal shells were taken from^[19,20]. These measurements concern a solid body and not an isolated atom. In Born computations a semi-empirical correction was added to such energy values and the contribution from type (4) processes was computed separately. In classical computations no such correction was introduced and the contribution from type (4) processes was accounted for automatically.

Figures 2 and 3 show the results of the computations. It is apparent that both the classical and quantum computations clearly reproduce the two peaks in the Ca, Sr, and Ba curves, and a single peak in the Mg curve in full agreement with the experiment. It is difficult to explain other details of experimental curves

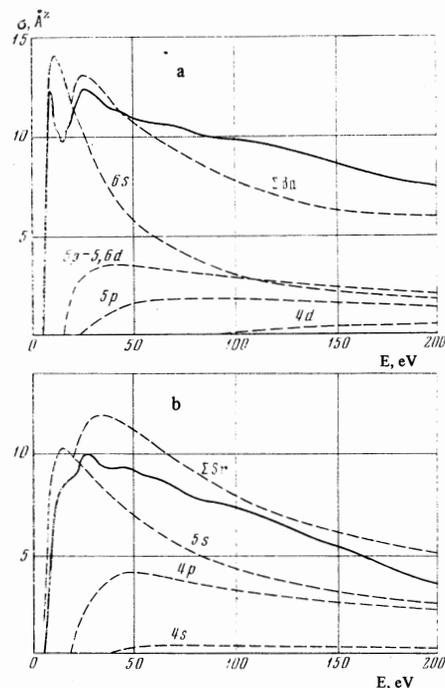


FIG. 3. Contribution from inner shells taken into account in Born approximation for Ba (a) and in binary approximation of classical mechanics for Sr (b). Solid lines are experimental results; Σ is the computed total cross section.

with a sufficient reliability for the lack of detailed information on the atomic structure; both the classical and quantum theories are not accurate enough to describe quantitatively the fine detail of the experimental curves. Nevertheless they may be naturally assumed to result from the superimposition of contributions from the processes discussed above (Fig. 3).

The only unexplained fact is that the first maximum of the experimental curve for Ba lies to the left of the theoretical maximum. We do not know of any other such case and it seems improbable that this discrepancy can be eliminated by a more accurate computation of the above processes.

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