

2. INTERNATIONAL
SUMMER SCHOOL
ON VACUUM PHYSICS 1974
COLLISION PHENOMENA
IN VACUUM

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PREFACE

This book contains the manuscripts (in some cases the abstracts only of the invited lectures given at the 2. International Summer School on Collision-Phenomena in Vacuum held at Fonyód. 23. September - 2. October 1974., organized by the Hungarian Roland Eötvös Physical Society, Budapest, Hungary.

The edition of this book was made possible by the helpful cooperation of the lecturers, who almost all sent their manuscript to the Editorial Committee of the School typed in the form used for the edition without retyping.

We hope the topics presented here on special aspects and problems of the collision processes in vacuo will be valuable to colleagues working in the field.

Thanks are due to the authors for their kind cooperation.

Program Committee

EXCITATION AND IONIZATION PHENOMENA IN LOW PRESSURE GASES

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ABSTRACT

The passage of electrons of sufficient energy through a gas will be followed by inelastic collisions of various kinds. The surplus of energy transferred from the incident electron to the atomic target can lead to the appearance of two main groups of detectable signals giving basic information on the gas conditions. These are: quanta of electromagnetic radiation and charged atomic particles.

Photons are created when an excited atomic particle decays to a lower energy level, the process being called deexcitation. The primary act is mainly the excitation collision of electrons with atomic particles of the gas. Processes occurring in such collisions are discussed and the importance of each of them analysed. Quantitative data are presented for some atoms of interest.

Charged atomic particles are formed if the energy transferred from the electron exceeds the minimum ionization potential of the target particle. The total and partial gas pressure measurements, as well as the gas composition analysis, are based on the detection of ions formed in ionizing collisions. Various processes leading to the formation of singly and multiple-ionized particles are discussed. Cross sections for some processes will be compared for a number of atomic species in order to show their importance in low pressure gases.

1. EXCITATION OF ATOMIC PARTICLES BY ELECTRON IMPACT

1.1. Excitation of an atomic particle

Under the excitation of an atomic particle (atom, molecule or ion) by electron collision a process is understood in which a part of the incident electron kinetic energy (E_i) is transferred to the target particle, the latter being excited to a higher energy state. Schematically this process can be represented as



where A_n^* denotes the excited atomic species, and $e(E_f)$ is the scattered electron having after the collision an amount of kinetic energy E_f , for E_n lower than the incident energy E_i . The value of the energy E_f depends on the energy amount transferred to the atomic particle. The energy conservation law for this process can be written in the form

$$E_{in}(A) + E_i + E_k(A) = E_{in}(A_n) + E_k(A_n^*) + E_f \quad (1.2)$$

where $E_{in}(A)$ and $E_{in}(A_n^*)$ are the atomic particle internal energies before and after the collision, respectively; $E_k(A)$ and $E_k(A_n^*)$ are the target particle kinetic energies due to the thermal motion. In most cases $E_k(A) = E_k(A_n^*)$ so that the relation (1.2) can be simplified to

$$E_{in}(A_g) + E_i = E_{in}(A_n^*) + E_f \quad (1.3)$$

The excited atomic energy state is not stable and after some time it decays to a lower lying energy level. If that lower level is not stable, too, the decay process will be continued until the atomic particle finds itself in the ground energy state. The internal energy decrease is mostly performed by the emission of radiation, and it is called the deexcitation process. Schematically it can be presented as

$$A_n^* + A_m^* + h \cdot \nu_{nm}, \quad (1.4)$$

ν_{nm} being the frequency of the emitted radiation. The energy conservation law for the deexcitation process is

$$E_{in}(A_n^*) = E_{in}(A_m^*) + E_{ph} \quad (1.5)$$

The excitation of the atomic particle by electron impact is the primary reaction, and the deexcitation is the secondary process. The analysis of equations (1.1) and (1.3) shows that there are two possibilities to detect the occurrence of an excitation process between the electron and the target particle. The first consists of energy analysis of the scattered electrons and of the determination of energy difference $E_n = (E_i - E_f)$. From E_n one can find out to which energy level the target particle was excited during the primary process. The detection of these electrons requires the application of

electron energy analysers, and the detection of scattered electrons, mostly in the single detection mode. The experimental technique of this sort is called the electron spectroscopy (Klemperer, 1965) (Siegbahn, 1972) (Carlson, 1972) (Steckelmacher, 1973).

The analysis of electrons and their detection has been recently developed, and it can be easily done in the laboratory. It is much more difficult to apply this method for the analysis of scattered electrons in non-laboratory conditions, such as for example in the case of the ionized gas analysis, extraterrestrial investigation, etc.

The second method for detecting an excitation process consists of energy analysis and detection of photons emitted from the excited atomic energy state. In principle this method is not straightforward since the excited state can decay into many lower lying energy levels giving birth to photons of different wave lengths. Nevertheless, the wavelength analysis of emitted photons enables the determination of the energy state excited in the primary process. The wavelength analysis and the detection of photons, mostly in the single detection mode, is called the photon spectroscopy.

The analysis of photons and their detection is a well known experimental method, and it can be efficiently used in the laboratory, as well as in any other circumstances. The analysis of photons is for example the most widely used method to determine the conditions of various gaseous discharges, including the extraterrestrial plasmas like the Sun and other light sources.

It is of interest to point out that although the detection of the photon emission is a very important source of information on the state of gaseous discharges and natural plasmas, the systematic investigation of excitation processes started some fifteen years ago and not too many reliable results do exist so far. The photon energy analysis was extended from the visible part of the spectrum to infrared, ultraviolet and the X ray regions in recent experiments.

1.2. Excitation cross section

We will introduce the concept of the excitation cross section by considering the propagation of an electron beam through a gaseous medium with the number density of atoms or molecules equal to N . Let us take that all

electrons have the same energy E_1 , and that the gaseous target contains only one atomic species. Schematically this is shown in Fig.1.1.

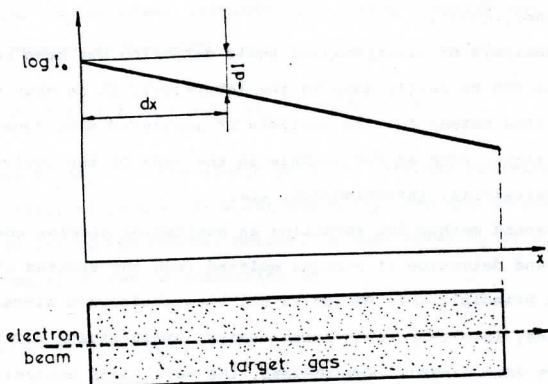


Fig.1.1.- Attenuation of the primary beam intensity during the passage through a gaseous target

At a point along the beam the intensity will be taken to be equal to I . After travelling a distance dx the decrease in the beam intensity will be

$$- dI = I \cdot N \cdot \sigma_t(E_1) dx \quad (1.6)$$

where $\sigma_t(E_1)$ is called the total cross section. It is a measure of the probability that an incident electron with energy E_1 will be scattered from the beam by the target particles. This cross section includes all possible processes which can cause the decrease of the primary beam intensity. Here we are interested only in some of these processes, namely in the excitation of the target particle to a well defined higher energy state. We will denote by $\sigma(E_1, E_n)$ the cross section for an inelastic process in which the incident electron of energy E_1 will collide with the target atom and transfer to it an amount of energy E_n , sufficient to excite it into a given higher energy state. For this case after the integration over the beam length, equation (1.6) will give

$$I_x = I_0 \cdot \exp[-\sigma_t(E_1, E_n) \cdot N x] \quad (1.7)$$

For low number densities N , when the mean free path of the electron is much

bigger than the experimental apparatus dimensions ($\lambda \gg D$), the exponential term can be expanded into a power series and all the members of it, except the linear one, disregarded. Then one comes finally to

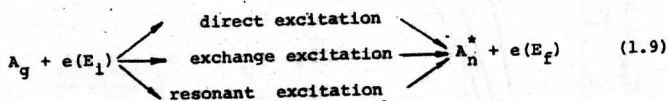
$$I_{\text{exc}} = I_0 \cdot \sigma(E_1, E_n) \cdot N \cdot x \quad (1.8)$$

Here I_{exc} is the intensity of the physical quantity giving signal that a particular excitation process occurred along the beam length x .

As already mentioned, there are two possibilities to detect an excitation process, namely by energy analysing and detecting the scattered electron intensity, or by detecting the deexcitation photon intensity previously analyzed to wave lengths. We will describe briefly both these possibilities.

1.3. Excitation processes

In equation (1.1) only the incident and the final products of an excitation process are included: on the left side the target atomic particle and the impinging electron, and on the right the excited atom and the scattered electron. This schematic representation does not say anything about the actual process of interaction and the possible reactions which may happen during the encounter. We will visualize these intermediate states by introducing them into equation (1.1). There are three possible and known channels for the reaction to happen:



1.3.1. Direct excitation

By direct excitation a process is understood in which the impinging electron interacts with the target particle and an amount of energy is transferred to it. The transfer mechanism can be represented schematically as in Fig.1.2.

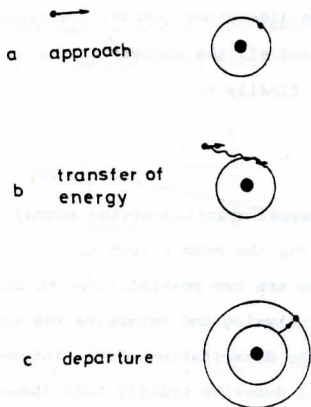


Fig.1.2.- Schematic representation of the direct excitation process

The probability of the direct excitation process is energy dependent, and it is usually a slowly variable quantity. In Fig.1.3. an excitation function

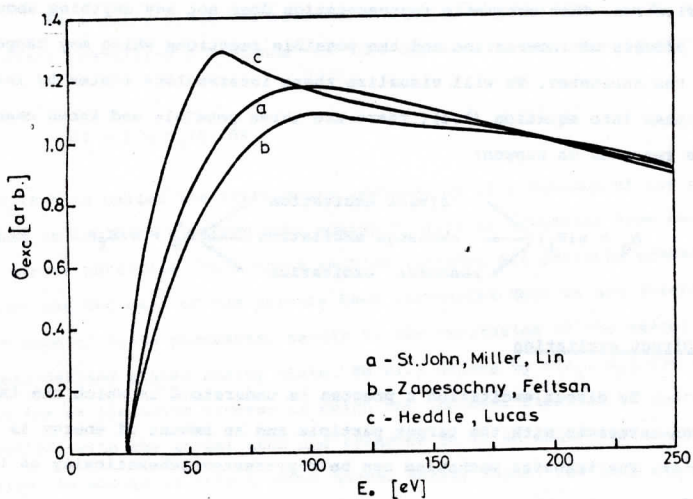


Fig.1.3.- Excitation functions for the 3^1P-2^1S state of helium obtained by various investigators, and normalized to the energy of 200 eV.

is given as an example for direct excitation energy dependence. As one can see even for this smooth curve appreciable differences do exist in the shapes obtained by various authors. Differences in cross section values are even bigger. According to the simplest explanation, the energy is transferred to one single electron of the target atom, the others being undisturbed. It is obvious that it is only a rough approximation, since any spatial change of atomic electrons will alter the overall potential distribution. Other electrons will find themselves in a different potential field, adjust themselves to it, and so they will take part in the excitation process.

1.3.2. Exchange excitation

While in the direct excitation only an amount of energy is transferred from the electron to the atom, in the exchange excitation an actual exchange of electrons does occur. We can visualize the process as in Fig.1.4. One can imagine the process as to have four steps. In the first the impinging

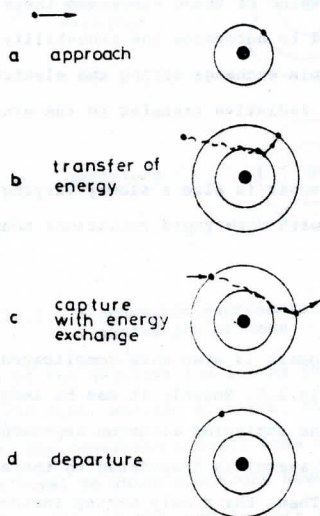


Fig.1.4.- Schematic representation of the exchange excitation process

electron is approaching the target atom with an energy E_1 . During the second step an amount of energy is transferred from the electron to the atom, and one of the atomic electrons is excited into a higher energy state, the incident electron being left with a small kinetic energy. Then, the incident electron is trapped inside the shallow potential well of the excited atom, while simultaneously the excited electron will leave the atom. The remaining electron, formerly the incident one, will be bound into one of the atomic excited energy levels.

The crucial difference between the direct and exchange excitation is that the electron remaining in the excited state was prior of interaction the incident electron, and that the scattered electron was prior to interaction bound to the atom. The so excited electron can have the spin in the same or in the opposite direction in respect to the ejected atomic electron. If the incident and ejected electrons have parallel spins, one can not distinguish by any known experimental method whether the atom was excited by a direct or exchange collision. For antiparallel spins of these electrons there are methods for measuring the spin flip, and to determine the probability for the exchange excitation. Thanks to this spin exchange during the electron-atom collision energy states forbidden for radiative transfer to the ground state can be excited.

The exchange excitation process is also a slowly varying function of the incident electron energy, but with more rapid variations than in the case of the direct excitation.

1.3.3. Resonant excitation

The resonant excitation process is even more complicated. Schematically it can be represented as in Fig.1.5. Roughly it can be imagined to happen in four steps. In the first, the impinging electron approaches the atom. During the second, an amount of energy is transferred to the atom and it is excited to a higher energy state. Then, the slowly moving incident electron with a kinetic energy close to zero, can be trapped by the excited atom in one of its energy states. For a period of time much longer than the transit time of the electron through the atomic potential dimensions, the new compound state of the negative ion will exist as a system. In the fourth step an internal energy exchange happens.

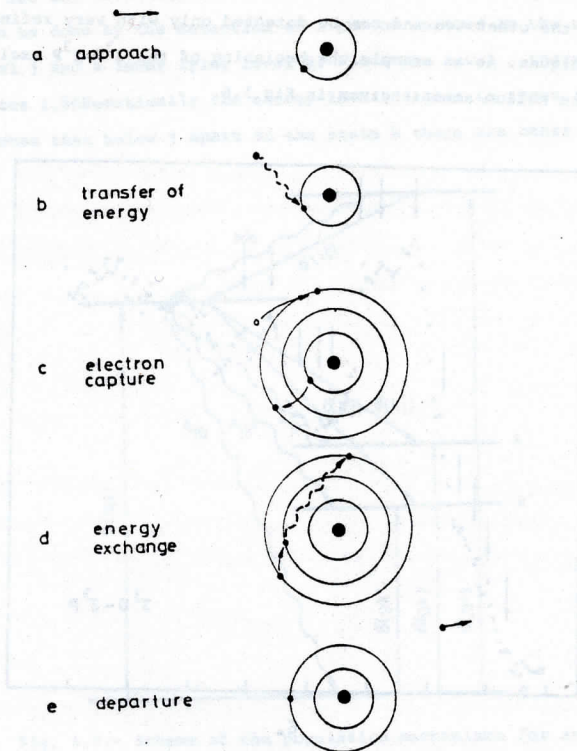


Fig.1.5.- Schematic representation of the resonant excitation process

One electron of the negative ion leaves the system with a kinetic energy transferred from the other excited electron, the latter falling into a lower lying energy state. The remaining neutral atom can be left in any energy level lower than the level to which electrons have been bound during the existence of the negative ion. If the atom is left in the ground state, the process is called the resonant elastic scattering, but if it is left in one of the possible excited energy levels, the process is called the resonant excitation.

The resonant excitation process may happen only for a definite electron energy, so that the probability for the process is finite in a very

narrow energy range, of the order of 50 meV, or less. This process occurs parallelly with the other two and can be detected only with very refined experimental techniques. As an example the beginning of the 3^3D-2^3P excitation function of the helium atom is given in Fig.1.6.

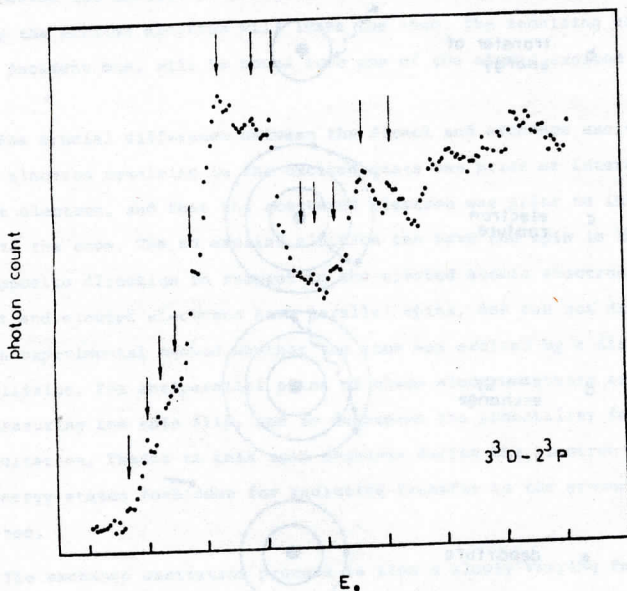


Fig.1.6.- Excitation function 3^3D-2^3P of the helium atom above threshold, showing resonant excitation features (Kurepa, Heddle and Keesing, 1974).

The 3^3D level could not be populated by cascading from upper lying levels, Only processes of collisional excitation to the 3^3D level could contribute to it's population. As one can see many resonant excitation processes have been detected, and some of them already identified.

1.4. Populational equilibrium of an excited energy state

We will consider now a simple case and see what can happen during the interaction of electron with an atomic species and which processes the population of a given energy level depends on.

Let the investigated atom have many energy levels, and let the investigation be done by the detection of a photon emitted in the transition between a level j and a lower lying level k . Above the level j there are other energy states i . Schematically the energy level diagram is shown in Fig. 1.7. Let us suppose that below j apart of the state k there are other energy states k' , too.

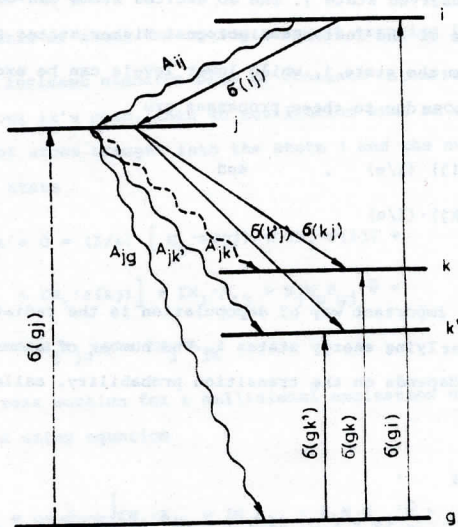


Fig. 1.7.- Scheme of the population mechanisms for an energy level.

In the collision of an incident electron with the atom, any of the higher energy states can be excited as long as the energy condition is fulfilled. The observed upper energy state taking part in the detected transition can be populated in many different ways. This level can be depopulated by more than one mechanism, too.

The most important process from the point of view of measuring the cross section is the collisional excitation of the observed energy state j . This excitation can happen through different mechanisms, as already mentioned earlier. In this analysis we will not distinguish between them, and we will include them all in the term collisional excitation. The population of the state j by collisional population depends on

$$+ N_g \sigma(gj) \cdot (I/e) \quad , \quad (1.10)$$

where $\sigma(gj)$ is the cross section for excitation of the level j from the ground state.

In other collisions some atoms can be excited into any state higher or lower than the observed state j . The so excited atoms can collide for the second time with one of the incident electrons. Higher states can be collisionally deexcited into the state j , while lower levels can be excited to the same state. Populations due to these processes are

$$+ EN_1 \cdot \sigma(ij) (I/e) \quad , \quad \text{and} \quad (1.11)$$

$$+ EN_1 \cdot \sigma(kj) \cdot (I/e) \quad (1.12)$$

respectively.

The most important way of depopulation is the radiative transition into one of the lower lying energy states k . The number of atoms deexcited by these processes depends on the transition probability, called Einstein coefficients A_{jk} :

$$- EN_j \cdot A_{jk} \quad . \quad (1.13)$$

The same applies to the higher energy levels, too. Some of them decay into the state j and increase it's population by

$$+ EN_1 \cdot A_{ij} \quad . \quad (1.14)$$

The excited atom has a finite life time. During this time it can collide with other atoms, which can be either in the ground or any excited state. Since the number of excited atoms is small, their influence can be neglected and only collisions with atoms in ground state should be taken into account. The population of the level j by this process is

$$+ N_j \cdot N_g \cdot S_{gj} \cdot \bar{v} \quad , \quad (1.15)$$

where S_{gj} is the cross section for the excitation transfer from an excited atom to an atom in the ground state, and \bar{v} is their relative velocity.

The photon emitted from an excited atom on it's way towards the detection system can be absorbed by other atom of the same species. This process

is called the resonant trapping. The number of atoms in the state j will be kept constant with time, but the spatial distribution of them will change. This will change the detectability of photons from the excitation process. The influence of this process on the j state population is

$$+ N_j A_{jg} Y \quad , \quad (1.16)$$

where y is the ratio of atoms undergoing resonant trapping in the gas.

If an incident electron beam of constant intensity is exciting the gas atoms along its path, then an equilibrium will be established between the number of atoms brought into the state j and the number of atoms leaving the same state

$$\begin{aligned} dN_j/dt = 0 = (I/e) \cdot [N_g \cdot \sigma(gj) + EN_1 \cdot \sigma(1j) + \\ + EN_k \cdot \sigma(kj)] + EN_1 \cdot A_{1j} + N_j N_g S_{gj} \cdot \bar{v} + \\ + N_j A_{jg} \cdot Y - EN_j \cdot A_{jk} \end{aligned} \quad (1.17)$$

The cross section for a collisional excitation of the state j can be thus evaluated using equation

$$\begin{aligned} \sigma(gj) = \frac{1}{N_g (I/e)} \left\{ EN_j \cdot A_{jk} - EN_1 A_{1j} - N_j N_g S_{gj} \cdot \bar{v} - \right. \\ \left. - N_j A_{jg} \cdot Y - \frac{I}{e} [EN_1 \cdot \sigma(1j) + EN_k \cdot \sigma(kj)] \right\} \end{aligned} \quad (1.18)$$

This equation contains all the data needed in order to determine quantitatively the cross section $\sigma(gj)$.

Fortunately somewhat smaller number of data are needed if the experiment is done under the single collision condition, i.e. when the mean electron path length is much bigger than the experimental apparatus. For this condition, one can introduce the following approximations

$$\left. \begin{aligned} N_j N_g S_{gj} \cdot \bar{v} &+ 0 \\ N_j A_{jg} \cdot Y &+ 0 \\ EN_1 \sigma(1j) &+ 0 \\ EN_k \sigma(kj) &+ 0 \end{aligned} \right\} \quad \text{for } (\lambda \gg D) \quad (1.19)$$

The equation (1.18) will be then simplified into

$$\sigma(gj) = \frac{1}{N_g \cdot (I/e)} \left\{ \sum N_j \cdot A_{jk} - \sum N_i \cdot A_{ij} \right\} \quad (1.20)$$

Even with this one has to know the contribution from all higher energy states, called the cascading processes.

1.5. Excitation functions

As it was shown in the preceding paragraph the excitation cross section determination is a difficult and tedious experimental task. This is the reason why a slightly simplified approach is used for quantitative description of the excitation process. Instead of measuring the cross section as a function of the incident electron energy, the intensity of photons emitted from the state j into the state k is measured as a function of the electron energy. The obtained quantity is called the excitation function or the apparent cross section. This function can be related to the cross section by the following way.

The intensity of photons emitted by the depopulation of the energy state j into the state k_1 depends on the transition probability between these states

$$I(jk_1) = A_{jk} \cdot N_j \quad (1.21)$$

If the number of atoms in the excited state j from (1.20) is substituted into (1.21) one gets

$$I(jk_1) = \frac{A_{jk_1}}{\sum A_{jk}} \left[(I/e) N_g \cdot \sigma(gj) + \sum N_i \cdot A_{ij} \right] \quad (1.22)$$

In the first approximation one can take that the state j is populated by collisional excitation only, i.e.

$$I(jk_1) = N_g \cdot \sigma'(gj) \cdot (I/e) \quad (1.23)$$

where $\sigma'(gj)$ is called the apparent cross section for the excitation of the state j from the ground state in collision with electrons. By substituting (1.23) into (1.22) one comes to

$$\sigma(gj) \cdot \frac{A_{jk_1}}{\Sigma A_{jk}} = \sigma'(gj) \left[1 - \frac{\Sigma I(ij)}{\Sigma I(jk)} \right] \quad (1.24)$$

where the relation

$$\frac{A_{jk_1}}{\Sigma A_{jk}} = \frac{I(jk_1)}{\Sigma I(jk)} \quad (1.25)$$

was used. The $\left[\frac{A_{jk_1}}{\Sigma A_{jk}} \right]$ is commonly referred to as the branching ratio of the $j \rightarrow k$ transition.

It can be seen that the excitation cross section $\sigma(gj)$ and the apparent excitation cross section $\sigma'(gj)$ have the same value if the upper energy state j of the observed transition is not populated by cascading from higher energy states i , and if the depopulation is happening into one lower lying energy state only. For cascading processes present, these two quantities are different in magnitude, the difference being dependent on the population of state j from upper lying levels i , as well as on the depopulation

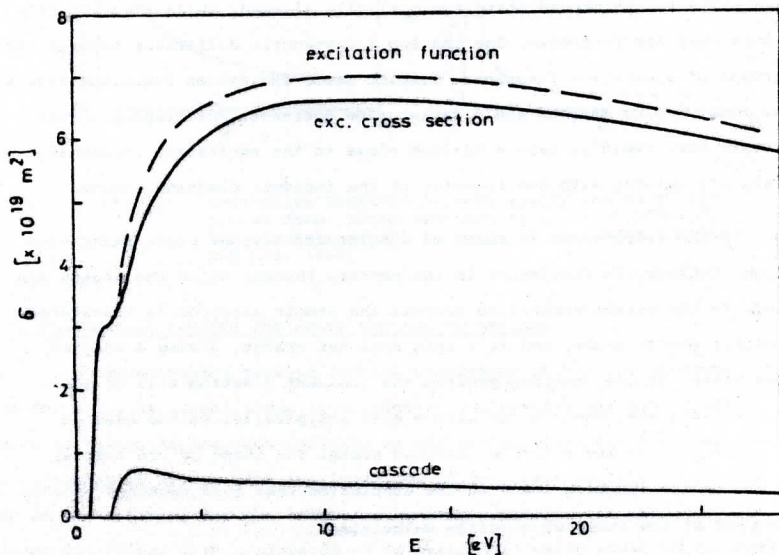


Fig.1.8.-The contribution of cascading processes to the excitation function from ^{52}P levels of rubidium (Zapsochny and Shimon, 1966).

of the state j into other lower lying levels k' . A careful analysis of cascading process contribution is shown in Fig. 1.8.

The state of art at the moment is such that most experimentalists are doing excitation function measurements, increasing so the amount of data, with hope that for some energy levels the absolute excitation cross section will be measured. Then all other available data will be normalized to this absolute cross section.

1.6. Excitation function shapes

For all energy levels the excitation functions do start at an electron energy equal to the threshold energy, rise, approach a maximal value, and then decrease with further increase of the electron energy. But the shape of excitation functions differs for various energy states, depending on whether the transition from the upper to the lower state are optically allowed or forbidden. This behaviour of excitation functions is shown for the helium atom in Fig.1.9. One should point out that optical transitions from the singlet state to the ground state are optically allowed, while from the triplet ones they are forbidden. One can see a systematic difference between the two groups of excitation functions. Singlet state excitation functions have a slower rise, a wide maximum and a rather slow decrease. For triplet states they start more rapidly, have a maximum close to the excitation threshold, and fall off quickly with the increase of the incident electron energy.

The differences in shape of singlet and triplet state excitation functions reflect the difference in the process through which the states are excited. In the direct excitation process the atomic electron is transferred to a higher energy state, and its spin does not change, giving a singlet excited state. In the exchange process the incident electron will be left in an excited state, when it can have a spin antiparallel to the ejected atomic electron, giving a triplet excited state. The shape of the triplet state excitation function leads to the conclusion that this exchange process is favoured at low incident electron velocities.

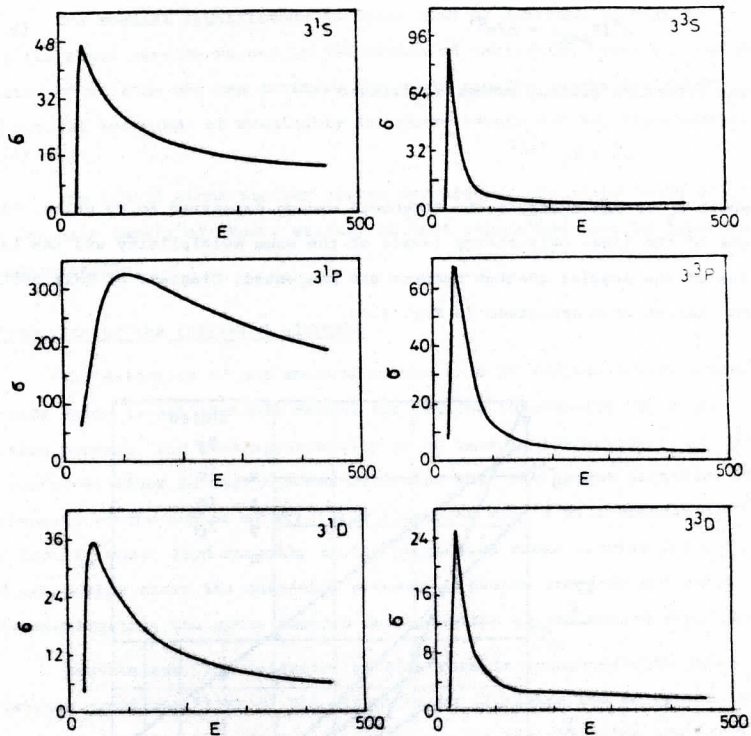


Fig.1.9.- Excitation function of some energy states of the helium atom. Cross sections in units of 10^{24} m^2 , the electron energy in units of eV (StJohn, Miller and Lin, 1964)

1.7. Exponential law for the cross section in maximum

Experimental results for the excitation of the helium atom, and for atoms of alkali atoms, too, show that a certain regularity does exist in values of the cross section at the maxima of excitation functions. If a diagram is drawn, with the logarithm of the cross section in the maximum as the ordinate and the effective quantum number as the abscissa, a linear dependence with a slope of -3 is obtained, which could be interpreted

$$\sigma^n(E_{\max}) = c/n^\alpha \quad (1.26)$$

The effective quantum number is defined

$$n^\alpha = E_C^{-1/2} \quad (1.27)$$

where E_C is the energy state threshold energy expressed in Ry units. Along one of the lines only energy levels of the same multiplicity and the same value of the angular quantum numbers are presented. Diagrams of this sort for the helium atom are given in Fig. 1.10.

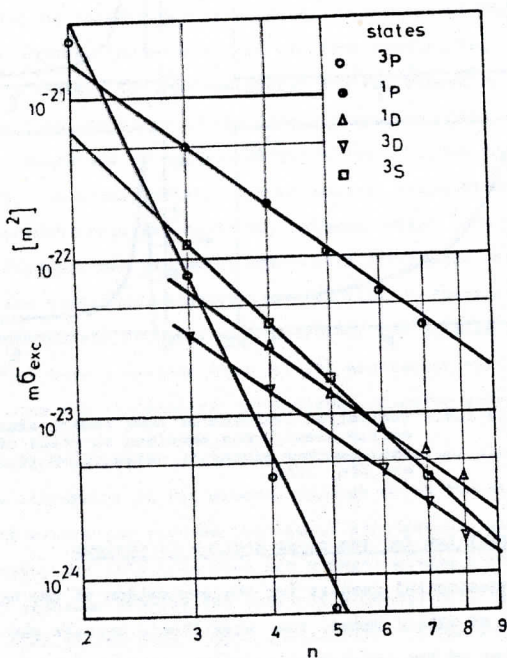


Fig.1.10.- Experimental verification of the E law for excitation cross section values in the maximum of the curve (Zapsochny, 1970)

The special significance of these kind of diagrams is that by knowing the cross section values in the maxima of excitation functions for a few states of an atom one can estimate the cross section values for other states not yet measured, or unsuitable for measurements for any experimental reason.

For alkali atoms similar curves were found, the slope being different for each family of energy states, so that this slope must be determined experimentally.

1.8. Detection of the scattered electron

The detection of the emitted photon from an excited energy state, as already said, is not the only method for getting information about the excitation process. The other possibility is to measure the intensity of electrons scattered after an excitational collision with the target particle. The determination of the number of scattered electrons with a well established energy loss E_n would lead directly to the excitation cross section and one would not bother about the cascading processes, photon trapping and other effects complicating the cross section determination by the photon detection.

Nevertheless, the detection of electrons is connected with other experimental problems. First of all, in order to determine the energy of the scattered electron and the amount of energy lost in the collision one has to have a very narrow energy distribution of the primary electron beam. Monochromators constructed in the last fifteen years have energy widths of the order 10-30 meV, which is still for two orders of magnitude worse than the energy resolution of the optical experiment. Further, with the increase of the principal quantum number of the energy state excited in the collision, the difference in the energy loss E_n for neighbouring levels decreases and it becomes increasingly difficult to separate them from each other. The monoenergetization and the post-collisional energy analysis of the scattered electron beam decreases the intensity to be detected to a level where integral methods can not be used any more. The scattered electrons have to be detected by a single counting technique. An experimental apparatus suitable for the analysis of the scattered electrons is shown in Fig.1.11.

The other main experimental problem is that so far no experimental technique does exist able to detect all electrons scattered after a definite

excitational collision, within a solid angle 4π . Instead, one has to measure the intensity of the electrons scattered into a solid angle $\Delta\Omega$ around an angle θ in respect to the primary beam direction, and the so obtained differential cross section integrate over the whole solid angle 4π .

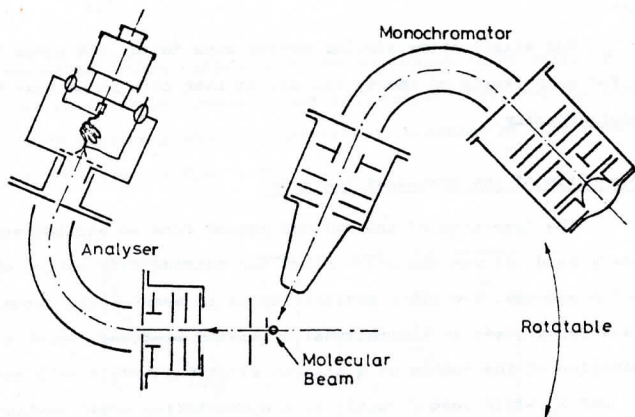


Fig.1.11.- Experimental arrangement for measuring angular distributions of inelastically scattered electrons by atom (Pavlović, Bonnes, Herzenberg and Schultz, 1972)

Examples of the differential cross sections for the excitation of He atom energy states is shown in Fig.1.12. Measurements of this kind are very complicated, but if done carefully, they can at the end give values of the excitation cross section for the process from the ground energy state of the target particle to a definite excited state. For the time being many experimentalists are doing this type of measurements, and new results do appear constantly.

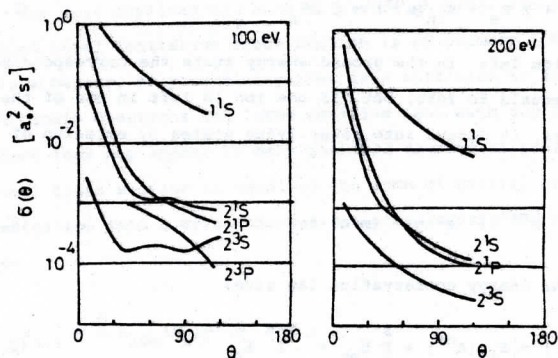
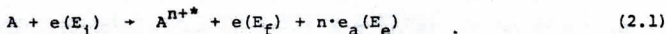


Fig.1.12.- Differential cross section for excitation of some energy levels of the helium atom (Suzuki and Takanayaga, 1973).

2. IONIZATION OF ATOMIC PARTICLES BY ELECTRON IMPACT

2.1. Ionization of an atomic particle

By the ionization of an atomic particle a process is understood in which the impinging electron transfers to the target particle an amount of energy sufficient to eject one or more electrons and leave it positively charged. This can be shown as



The n times positively charged ion can be in its ground state or any of the possible excited states. The ejected electrons have in principal different energies (E_e), and leave the scattering volume at different angles in respect to the primary beam direction. The energy conservation law for this case can be written as

$$E_k(A) + E_{in}(A) + E_i = E_k(A^{n+}) + E_{in}(A^{n+}) + E_f + \sum^n E_e + \sum IP_n \quad (2.2)$$

Here IP_n stands for ionization potential of the n -th electron. If the target particle in the collision is an atom the change of its translational kinetic energy can be neglected so that (2.2) can be simplified

$$E_i = E_f + \sum^n E_e + E_{in}(A^{n+}) + \sum^n IP_n \quad (2.3)$$

For an ion left in the ground energy state the corresponding term in equation (2.3) equals to zero. But, if the ion is left in one of the possible excited states, it decays into lower lying states by emission of radiation, shown by

$$A^{n+*} \rightarrow A^{m+} + s \cdot h\nu + (m-n) \cdot e \quad (2.4)$$

For this process the energy conservation law gives

$$E_{in}(A^{n+*}) = E_{in}(A^{n+}) + \sum^s E_{ph} + \sum^{m-n} E_e \quad (2.5)$$

Here again, the ionization process, irrespective of how complicated it might be, will be called the primary process, while the emission of radiation and the ejection of subsequent electrons will be called secondary processes.

2.2. Ionization cross section

The ionization cross sections, similarly to the excitation cross section, is a measure of the probability that an electron will create a positively charged particle in a collision with the atomic particle. The connection between the number of ions formed with a degree of ionization n and the number of incident electrons is given by

$$N_{ion} = (I_0/e) \sigma_{ion}(E_i, n) \cdot N \cdot x \quad (2.6)$$

This equation is a particular solution of the most general equation (1.6).

The cross section for formation of an ion with a positive charge (ne) is usually called the partial cross section. In order to obtain the cross section for the ionization into a given charged state one has to determine the number of ions formed. Measurements are done mainly by the current determination, in which case a correction for the number of elementary charges of the ion must be introduced into equation (2.6)

$$\sigma_{ion}(E_i, n) = \frac{1}{n} \frac{I_{ion}}{I_0} \frac{1}{N \cdot x} \quad (2.7)$$

For most applications such as plasma physics, vacuum physics etc, the so called total ionization cross section is of primary interest. This quantity is a measure of probability that in a collision an incident electron will eject atomic electrons and form positive ions with any degree of ionization. Since ions may appear in many possible degrees of ionization, the so defined total cross section is equal to the sum of partial cross sections for the ionization into a given charged ion state multiplied by the ionization degree

$$\sigma_{i,t} = \sum^n \sigma_{ion}(E_i, n) \cdot n \quad (2.8)$$

The first member of the sum is the cross section for ionization into singly charged ion. This is the most probable ionization event, and the total ionization cross section does not differ significantly from the single ionization partial cross section of the atomic particle.

2.3. Ionization processes

Like in the case of excitation, the schematic equation of the ionization (2.1) does not say anything about the physical processes happening during the interaction of the electron leading to the ejection of one or more electrons from the atomic particle. There are many possible processes giving charged atomic particle as the final product. We will discuss them briefly.

2.3.1. Single ionization by outer electron ejection

The simplest and energetically the lowest ionization process is the ejection of the most loosely bound atomic electron, called usually the valent electron. The energy balance equation (2.2) has for this case the following simple form

$$E_i = E_f + E_e + IP_1 \quad (2.9)$$

i.e. the difference between the incident electron energy and the ionization potential is shared by the scattered (E_f) and the ejected (E_e) electrons. The value of the ionization energy (IP_1) in tables corresponds to the lowest value of the incident electron sufficient to eject one atomic electron. The process

could be imagined to happen in three steps, shown in Fig.2.1. The first is the approach of the impinging electron. During the second step this electron

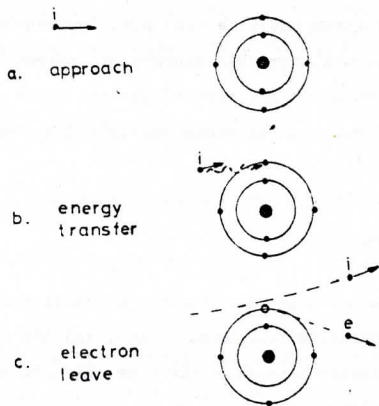


Fig.2.1.- Schematic representation of a single outer electron ejection in the ionizing collision

reaches the range of the target particle potential and an amount of energy is transferred from the electron to the target. If the transferred energy is equal to or higher than the atomic electron bounding energy, this electron will be ejected from the atom. During the motion of the ejected electron away from the rest of the atom it will interact with the incident electron, and they will share the amount of energy equal to the difference of the primary electron energy and the ionization potential.

A typical example of undisturbed process of this kind can be found in the case of the hydrogen, as well as in the helium atom in a limited energy range above the ionization threshold. In Fig.2.2. the ionization cross section curve for the hydrogen atom is given, showing a gradual and smooth rise as a function of the incident electron energy.

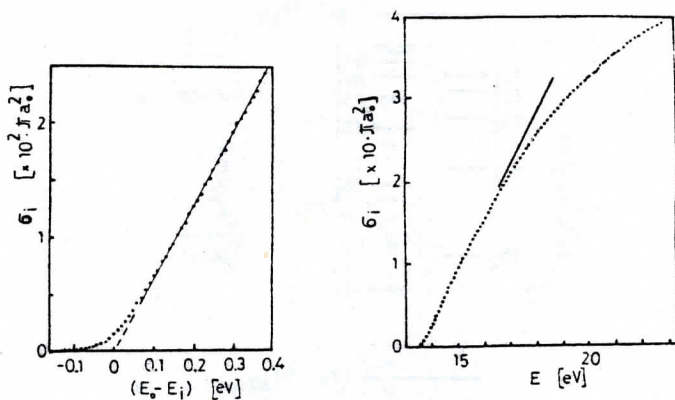


Fig.2.2.- The hydrogen atom ionization cross section curve in the threshold region (Mc Gowan and Clarke,1968).

2.3.2. Preionization of an excited outer electron

The most weakly bound electron is usually not the only one in the outer shell of the atom. Let for an example take the xenon atom, with the outer shell structure of $(5s^2 5p^6)$. From this ground atomic state one can eject electrons with various spin orientations in respect to the angular momentum of the orbit left vacant. The remaining electron can have a spin parallel or antiparallel to the angular momentum of the orbit occupied, so that the total angular momentum can have values of $j=1/2$ and $j=3/2$. Energies needed to eject the complementary electron are not the same, being higher for formation of an ion in the $j=1/2$ state. Different are also the energies for the excitation of electrons with spin orientations parallel or antiparallel in respect to the vacanted orbit angular momentum. To the excitation of these two electrons different energy terms can be assigned, approaching the corresponding energy limits. In Fig.2.3. the energy diagrams of states above the lower $2P_{3/2}^0$ ionization state are shown.

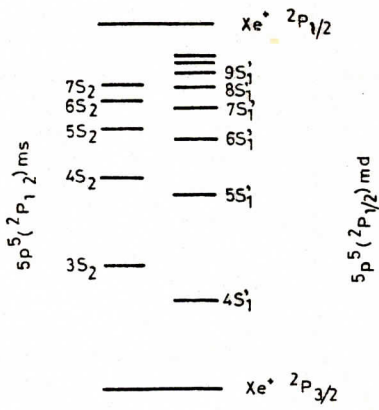


Fig.2.3.- Energy terms of the xenon atom above the $2P_{3/2}^0$ ionization limit.

All the excited states above the lower ionization limit are energetically unstable, so that an energy transfer occurs.

The whole process can be shown as to happen in five steps. The first one is the approach of the impinging electron. During the second one the electron enters the target particle potential field, and transfers to it an amount of energy sufficient to excite an electron to a higher energy state. If this happens to be one of $4p^5$ md states lying above the $j=3/2$ ionization limit an internal energy transfer will occur in the third step. This we could imagine to happen so as if that the excited electron is returned to its ground state, and the transition energy transferred to the other electron of the same atom with lower ionization energy. Finally, the ejected electron will carry away the surplus as kinetic energy.

The existence of the preionization processes can be detected as changes in the slope of ionization cross section curves in the vicinity of the ionization threshold for many atoms. As an example the ionization cross section curve of the xenon atom is given in Fig.2.5. The excitation of an excited state preionizing into the ground state of the ion starts at the

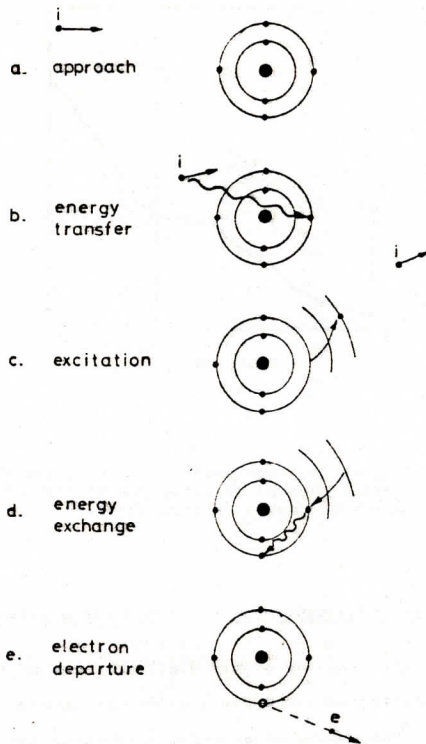


Fig.2.4.- Schematical representation of the preionization of an excited outer electron.

threshold and rises with the increase of the incident electron energy. The measured singly charged ion cross section is in this case a sum of excitation cross sections into states preionizing and the ionization for the direct ejection of the most weakly bound electron

$$\sigma_{\text{ion}}(E_0, l) = \sigma_{\text{ion}}(E_0, l)_{\text{dir}} + \sum \sigma_{\text{exc}}(E_0, i, l) \quad (2.10)$$

where i stands for the excited state.

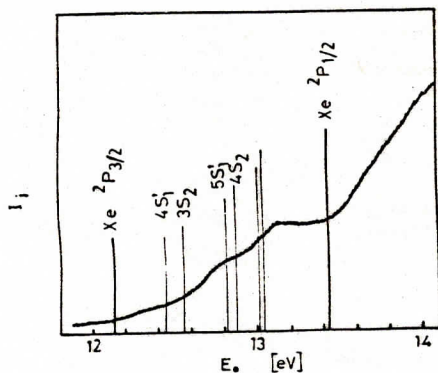


Fig.2.5.- Ionization cross section curve of xenon showing changes in slope due to preionization processes (Burns, 1964).

2.3.3. Preionization of two simultaneously excited outer electrons

This process involves two atomic electrons, one of them being ejected at the end of the interaction. One can imagine the process to happen in five steps. In the first the impinging electron approaches the atomic particle. During the second it enters the region of the interaction potential, and an amount of energy is transferred to the target particle. This energy is shared by two electron excited simultaneously into bound energy states. The total transferred energy exceeds the minimal energy needed to eject one atomic electron. In the fourth step an internal energy transfer occurs between excited electrons. One of them falls to its ground state, or possibly to an excited state of the ion, the transition energy being transferred to the other electron. This then leaves the system and becomes a free electron. Schematically this process is shown in Fig. 2.6.

The major difference of the two-electron preionization process in respect to the two previously mentioned ones is that it is a resonant pro-

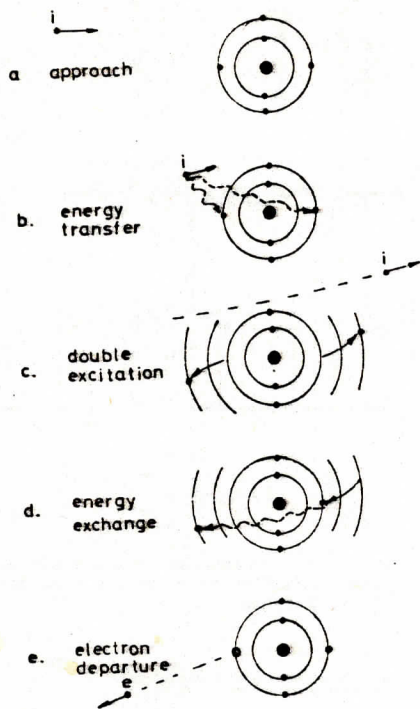


Fig.2.6.- Schematic representation of the preionization process of two excited electrons

cess. The primary electron can excite simultaneously two electrons at a definite energy only, the probability for the transfer being different from zero in an energy interval of the order of a few meV. Due to interference of this resonant process with other smoothly changing processes it can be detected as a Fano shape on the ion intensity curve, such as the one given in Fig.2.7.

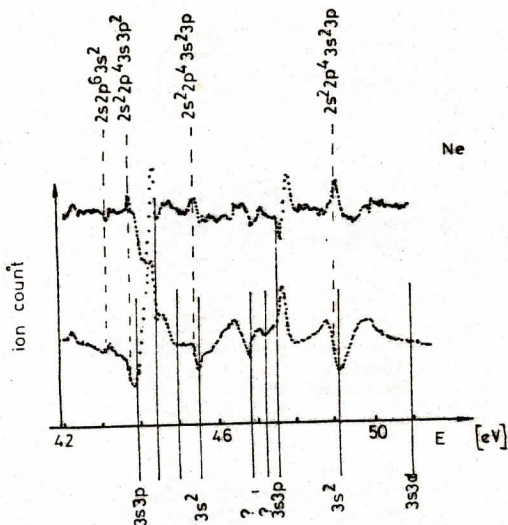


Fig.2.7.- Two-electron preionization processes detected on the ionization curve of the neon atom (Bolduc, Quémener and Marmet 1972).

2.3.4. Ionization through negative ion formation

In paragraph 1.3. the resonant excitation mechanism was explained, which goes through the formation of an unstable negative ion. The same process can lead to the ejection of one of the atomic electrons during the rearrangement period, if the energy condition is fulfilled. As an example we will consider the neon atom because there are experimental evidences that this process does exist. Schematically the process can be imagined to happen in five steps. During the second step the impinging electron transfers an amount of energy to the atom and two atomic electrons are excited. The incident electron can be capture into the excited atom to form an unstable negative ion. The total energy shared by the two excited atomic and the captured incident electron can be higher than the ionization potential. In the next step the total excitation energy will be interchanged between the three electrons, one of them falling to a lower energy state and the other two leaving the system.

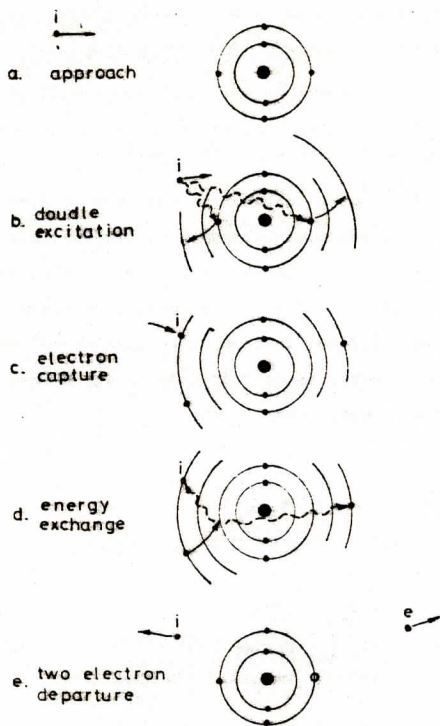


Fig.2.8.- The schematic representation of the ionization through negative ion formation.

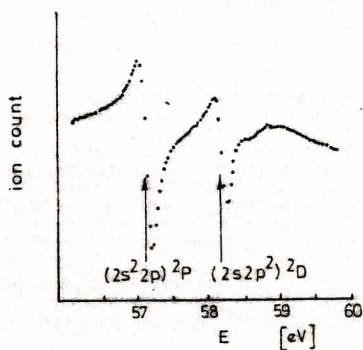


Fig.2.9.- The helium atom ionization curve showing processes of negative ion formation followed by ejection of two electrons (Quémener, Paquet and Marmet, 1971).

An experimentally obtained ionization function showing resonances at energies satisfying the above explanation is shown in Fig.2.9.

2.3.5. Multiple ionization by direct ejection of electrons

The process of direct energy transfer to two or more electrons simultaneously, followed by their ejection is possible, too. In this case the amount of energy transferred to the atom has to be greater than the total energy needed for the ejection of n atomic electrons. Schematically the process can be shown as in Fig.2.10. In fact, the experimental evidence suggests that the transferred energy is carried away mainly by one of the electrons, the others having an energy close to zero.

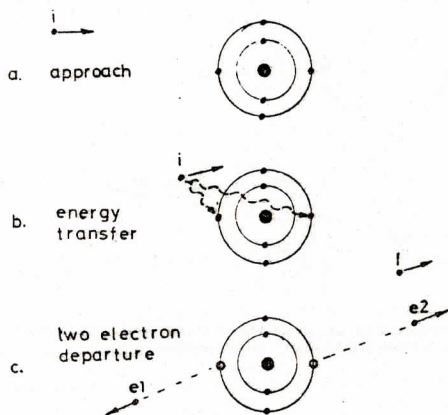


Fig.2.10.- Multiple ionization by direct electron ejection.

According to the theory, the ionization cross section for the multiple ionization by direct ejection of electrons should obey in the vicinity of the threshold a $(E_i - E_{ion})^n$ law, where E_{ion} stands for the binding energy of ejected electrons (ionization potential for ionization into n -charged state of the ion). Some experimental verifications of this law do exist.

Experimental determination of the oscillator strength for the doubly and triply ionized argon atom is shown in Fig.2.11. proving that the process of simultaneous ejection of two or three electrons, respectively, is a smooth function of the incident electron energy, and that mostly 3p electrons are ejected of the argon atom.

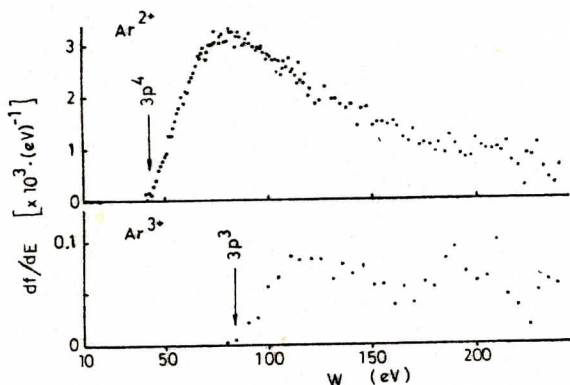


Fig.2.11.- Oscillator strength of the argon atom double and triple ionization by direct electron ejection (van der Wiel and Wiebes,1971).

2.3.6. Inner electron ejection followed by Auger processes

The ejection of an electron from the inner energy level can lead to many secondary processes. We will consider here the so called Auger-process only.

Schematically the process can be represented as in Fig.2.12. During the primary interaction the incident electron ejects one of the inner shell electrons, leaving the target particle as a singly charged ion. The ejected electron has been strongly bound so that the ion formed is energetically unstable. One other electron, from a higher lying energy state, will be transferred to the vacancy. The difference in binding energies can appear in the form of radiation, known as the characteristic X radiation of the atom. If this happens, the remaining ion will be singly ionized. The other possibility is that this amount of energy is transferred to other electrons

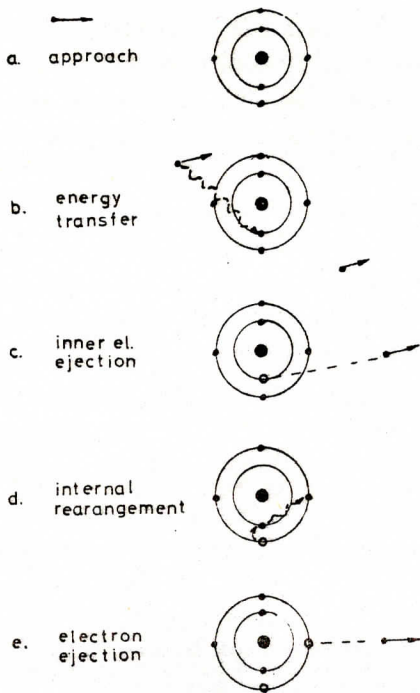


Fig.2.12.- Inner shell electron ejection followed by Auger process.

of the same atom. These electrons will leave the ion, so that a multiple charged ion will be formed at the end of these transitions.

Experimentally the existence of the described process can be detected by measuring the multiple charged ion intensity as a function of the incident electron energy. A particular ion species appears for the first time when the electron energy is just above the lowest ionization potential for the creation of this species. The ejection of an inner electron followed by the emission of $(n-1)$ secondary electrons can start at higher energies, and it can be observed as changes in slope and or shape of the ionization curve.

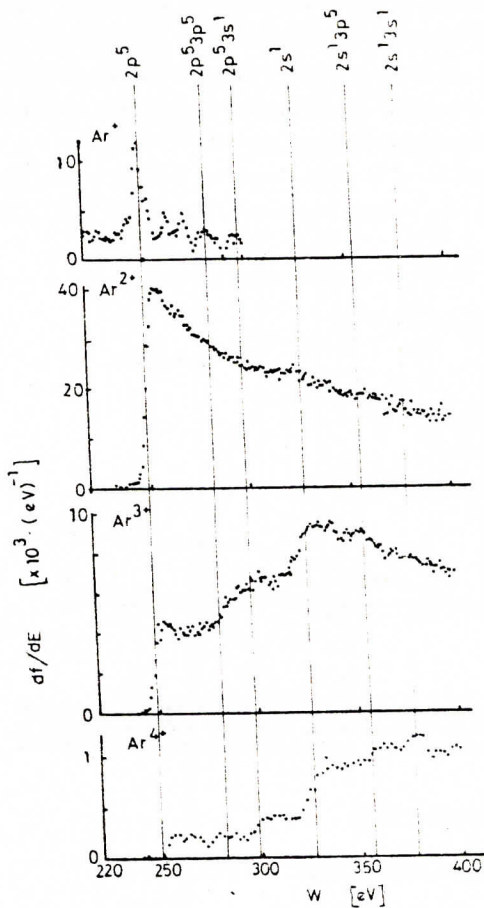


Fig.2.13.- Oscillator strengths of the argon atom for formation of ions through L shell ionization (van der Wiel and Wiebes, 1971).

More data were obtained by applying the electron-ion coincidence technique in order to measure the oscillator strength for the formation of ions in various charged states. Results of this sort are shown in Fig.2.13, for ion charges from one to four. The vacanted energy states during the pri-

mary interaction are marked on the drawing. As one can see at the energy where a new channel opens the curve changes its shape or slope.

It is very instructive also to observe the change of the probability that an ion with a certain charge will be formed after a well defined primary process, which is given in Fig.2.14.

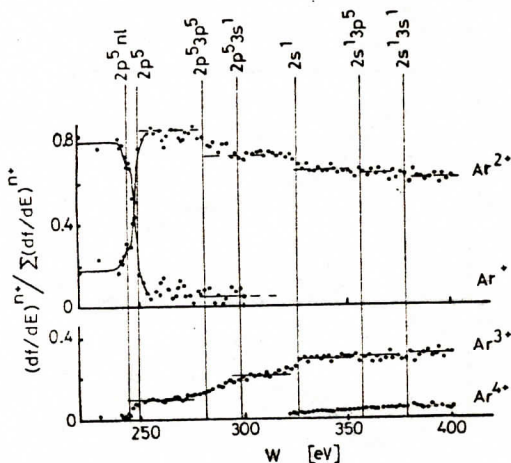


Fig.2.14.- Probabilities for the formation of n-charged ions of the argon atom for a given energy transfer E_n (van der Wiel and Wiebes, 1971).

2.4. Total ionization cross section

2.4.1. Total ionization cross section data

The total ionization cross section of various atomic species has been measured by many authors (for references see: Kieffer and Dunn, 1966), and it is still the object of interest.

It is of primary interest to point out that the discrepancies between cross section values obtained by different authors are mainly due to the uncertainty of the target gas pressure measurement. Until recently most authors used the McLeod gauge as an absolute standard for the measurement of the target gas pressure. Lately, other means were introduced, such as the

capacitance manometer, the gas expansion method and the constant gas flow method. Results obtained with these pressure measuring methods gave total ionization cross section values lower than the earlier data. The consistency of the new results (Rapp and Englander-Golden, 1965) (Fletcher and Cowling, 1974) (Kurepa, Čadež and Pejčev, 1974) brings us to the conclusion that new data do not differ significantly from the real values of total ionization cross sections. In Fig.2.15. a set of total ionization cross section curves is given.

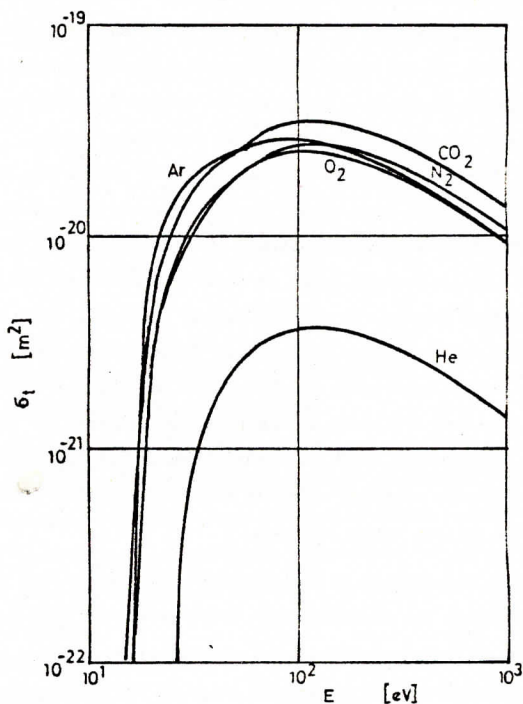


Fig.2.15.- Total ionization cross sections of main constituents of the normal atmosphere (Rapp and Englander-Golden, 1965).

2.4.2. Gas pressure measurement by ionization gauges

Between the total ionization cross section and the ion current in the electron-target particle collision experiment a linear correspondence exists, the coefficient being dependent on the gas pressure. That means that

by knowing the total ionization cross section of a given gaseous species the pressure of this gas could be determined by measuring the intensity of the ion current formed by the passage of the electron beam. This idea was tried by Klopfer (1961) and Kurepa and Kurepa (1965), and it was shown that it can be applied for pressure determination. Unfortunately in order to be able to measure the gas pressure by this method to a high degree of accuracy, one has to have tabulated total ionization cross sections determined to the same degree of accuracy or better, not available at that time. On the other side, only in a relatively small number of experiments the absolute value of the gas pressure is needed. In the great majority of experiments only a rough measure of the gas pressure is needed, which can be achieved using simpler and commercially available instruments, such as the ionization gauge.

In ionization gauges the basic signal on the gas pressure is obtained by collecting the ions formed in the electron-target atomic particle interaction. The main difference between an electron-target particle collision experiment and the ionization gauge is that by the latter the electrons do not have a well defined energy. It changes during the oscillatory motion of the electron between the filament and the ion collector. In Fig.2.16. the cross section of an ionization triode is shown with the path of the electron, from its emission from the filament to the place it collides by ionizing the target particle. The drawing gives also the shape of the total ionization cross section curve for the nitrogen molecule within the energy interval the electrons in the ionization gauge can have.

The interaction of the electron with the target molecule can happen at any energy of the electron. The signal obtained from a great number of electrons will in fact be proportional to the averaged value of the total ionization cross section in the energy interval defined by the filament-grid potential difference. The length of the electron path in an ion gauge depends on its dimensions, geometrical arrangement and so forth. Instead of applying the tabulated total ionization curves, manufacturers measure experimentally the signal intensity corresponding to a known gas pressure. The characteristics of the gauge are referred to as the gauge sensitivity, which includes the effective length of the electron path, the geometrical arrangement of the electrodes, and the ionization cross section.

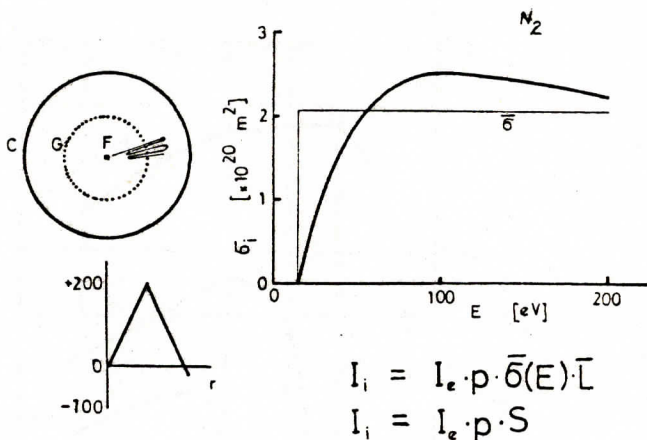


Fig.2.16.- Motion of the electron in an ionization gauge and the effect of this motion upon the signal of the pressure.

2.5. Partial ionization cross section measurements

2.5.1. Partial ionization cross section data

In order to determine the partial ionization cross section one has to mass-analyze the ions created in collisions of electrons with the target particle. In comparison with the total ionization cross section measurements, this experiment is much more complicated. Comparisons of results obtained by various authors show that discrepancies are very great, and that so far no reliable data do exist.

Results for the xenon atom are shown in Fig.2.17. One can see that processes of multiple ion formation start to be important even for electron energies of 100 eV.

2.5.2. Partial gas pressure analysis

Partial ionization cross sections are directly connected to the known mass spectrometric method for the partial gas pressure analysis. Each gaseous species in a closed container will give a set of ions with different

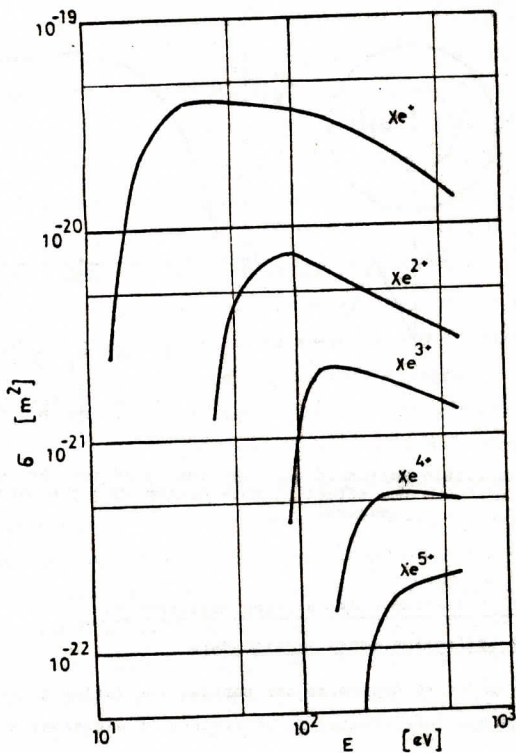


Fig.2.17.- Partial ionization cross sections of the xenon atom (Tate and Smith, 1934, normalized to total ionization cross-section at 30 eV of Rapp and Englander-Golden, 1965).

M/q values, the intensity of each ion species being proportional to the partial cross section for the formation of that ion in the electron-target particle collision. A mass spectrometric analysis of ions formed by the electron beam of definite energy, will provide a picture of relative intensities of ions. This will enable to identify the parent atomic particle present in the system, and the qualitative compositions of the gas. After careful calibration, even quantitative analysis of the gaseous atmosphere in a closed vessel can be performed.

In Fig.2.18. a mass spectrogram of the air obtained by a quadrupole mass filter in our laboratory is presented.

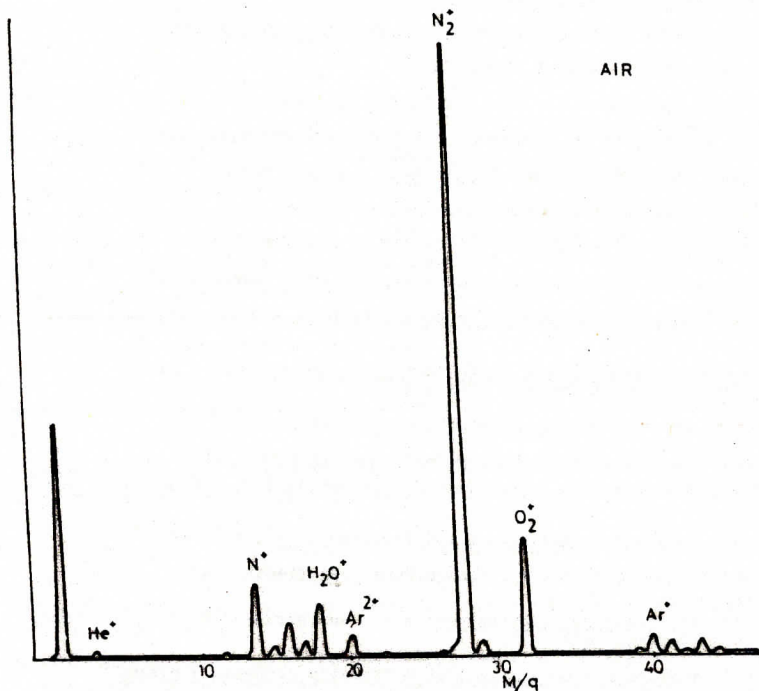


Fig.2.18.- A mass spectrogram of the air obtained by a quadrupole mass-filter.

References

- Bolduc E., Quémener J.J. and Marmet P.: J.Chem.Phys., **57**(1972)1957
- Burns J.F., Proc.3rd ICPEAC, London,1963. North Holland Publ.Co.1964,Amsterdam
- Carlson T.A., in "Electron spectroscopy" pp 53-57., ed.Shirley D.A.North Holland Publ. Co, 1972. Amsterdam
- Excitation électroniques d'une vapeur atomique - Application a la spectroscopie, CNRS, Paris, 1967
- Fletcher J. and Cowling I.R., J.Phys.B: Atom.Molec.Physics **6** (1973) 258

Heddle D.W.O., in "Atomic and Electron Physics - Atomic Interactions, Part A" pp 43-67, ed. Bederson B and Fite W.L. Academic Press, New York, 1968

Heddle D.W.O. and Keesing R.G.W. in "Atomic and Molecular Physics" pp 267-298 ed Bates D.R. and Estermann I. Academic Press, New York, 1968

Heddle D.W.O. and Lucas C.B., Proc. Roy. Soc. A271 (1963) 129

Kieffer L.J., Atomic Data 1 (1969) 121

Kieffer L.J. and Dunn G.H., Rev. Mod. Phys., 38 (1966) 1

Klemperer O., Reports on progress in physics, XXVIII, p.77, 1965

Klopfner A., Vac. Symp. Trans., Am. Vac. Soc. 1 (1961) 439

Kurepa J. and Kurepa M., JUVAK, 1965, Bilten br. 7

Kurepa M., Čadež I., and Pejčev V., Fizika, 6(4) (1974)

Kurepa J., Heddle D.W.O. and Keesing R.K., VII SPIG, Rovinj, 1974

Leck J.H., Pressure measurements in vacuum systems, Chapman and Hall Ltd. London 1964

Massey H.S.W., Electronic and Ionic Impact Phenomena, Vol. 1 and 2 At the Clarendon Press, Oxford, 1968 and 1969.

McGowan J.W. and Clarke E.M., Phys. Rev., 167 (1968) 43

Moiseiwitch B.L. and Smith S.J., Rev. Mod. Phys. 40 (1968) 238

Pavlović Z., Bonnes M.J.W., Herzenberg A. and Schulz G.J., Phys. Rev., A6 (1972) 676

Quémener J.J., Paquet C. and Marmet P., Phys. Rev., A4 (1971) 494

Rapp D. and Englander-Golden P., J. Chem. Phys., 43 (1965) 1464

Siegbahn K., in "Electron spectroscopy" p 53, ed. Shirley D.A. North Holland, Publ. Co., Amsterdam, 1972

Smirnov B.M. Atomije stolknovenija i elementarnije processi v plazme, Stomizdat, Moskva 1968

Steckelmacher W., J. Phys. E: Sci. Instr. 6 (1973) 1061

StJohn R.M., Miller F.L. and Lin C.C., Phys. Rev., 134 (1964) A 888

Suzuki H. and Takanayaga T., Abstracts of papers, VIII ICPEAC, p 286, Institute of Physics, Beograd, 1973

Tate J.T. and Smith P.T., Phys. Rev., 46 (1934) 773

Van der Wiel M.J. and Wiebes G., Physica, 53 (1971) 225

Zapesochny I.P. and Shimon L.L., Opt. Spectry (USSR) 21 (1966) 155 (encl. trans)

Zapesochny I.P. and Feltsan P.V., Urk. Fiz. Zh. 11 (1965) 1197

Zapesochny I.P. in "Physics of Ionized Gases", Proc. V SPIG, Herceg Novi, ed. Navinšek B., Institute Jožef Stefan, Ljubljana, 1970.