ATOM AND ION SOURCES

by

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1802014366

AKADÉMIAI KIADÓ · BUDAPEST 1977

1.2 IONIZATION OF ATOMS AND MOLECULES

Atomic or molecular ionization can be regarded, similarly to the excitation processes, as a change of the atomic molecular states.

Ionization is a process in which the atomic or molecular electrons are brought from the discrete energy state to a state contributing to the continuous spectrum, that is, one or more electrons escape from the atom or molecule. As a result of ionization, the originally neutral atom or ion with charge n transforms to an ion with charge m or $n + m$ with the simultaneous emission of m free electrons.

Atoms or molecules can be ionized by electron, atom or ion impact, by irradiation, or by exposure to an electric field.

1.2.1 IONIZATION OF ATOMS OR MOLECULES BY ELECTRON IMPACT

Inelastic collisions of atoms or ions with electrons can lead to ionization if the energy needed for the ejection of one or more electrons is imparted in the collision by the striking electron to the atom or molecule. The amount of energy needed for electron ejection depends on the given energy state of the colliding atoms or molecules.

Let E^i_{nl} be the minimum energy required for the ionization of an atom or a molecule in either the ground or any excited state (n is the main and l the orbital quantum number). This energy corresponds to the binding energy of the electron at the energy level in question. The energy E^i (see Appendix, Tables 3 and 4) required for ionization from the ground state is called the ionization potential.

Ionization occurs if the energy of the electron which makes an impact on the atom or molecule exceeds the value of E^i_{nl}.

It should be noted that it is possible for ionization to take place even at impact electron energies below the value of the ionization potential. This happens when the atoms or molecules are brought to an excited state by electron impact, then struck again by electrons during the lifetime of the excited state and eventually becoming ionized.

Similarly to the excitation cross section, the ionization cross section σ^i_{nl} is zero at impact electron energies $E_e \leq E^i_{nl}$. The cross section for single ionization σ_i is a function of the impact electron energy. This function is called the ionization function of the molecule. If $E_e = E^i_{nl}$ the ionization function shows a sharp threshold.

The ionization cross section increases with increasing impact energies and its value close to the ionization threshold can be predicted for single ionization of the atoms from the formula [70]

$$\sigma_i = C(E_e - E^i_0) \tag{1.18}$$

where C is a constant. In this expression the interaction between the striking and the ejected electrons has been ignored. A more precise formula has been reported [71] in order to take account of this interaction by modifying the exponent in (1.18) from 1 to 1.1269 for the ionization of atoms, and to 1.056

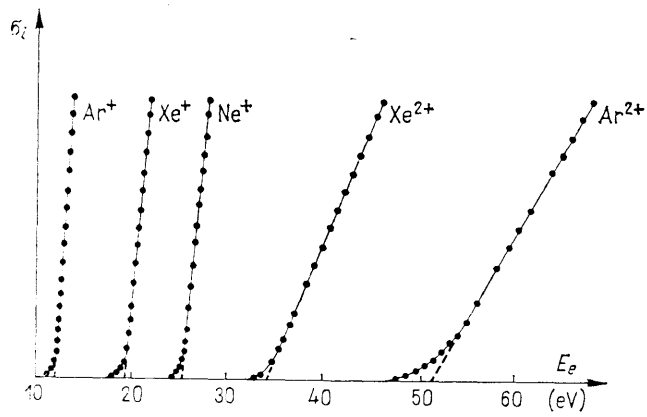

Fig. 1.19 Variations of ionization cross section values of argon, xenon and neon atoms with impact electron energies at values near the threshold energy

for that of ions. This small difference cannot be established from the experimental results available to date, thus for practical purposes it is reasonable to assume that the ionization cross section for a multiple ionization by, for example, a factor of n, can be predicted at impact energies near the ionization threshold as

$$\sigma_n^i = C(E_e - E_0^i)^n \tag{1.19}$$

The energy dependence of σ_n^i at impact energies near the threshold value as described by (1.19) has been confirmed in a number of experiments [4, 72–80]. For hydrogen atoms the prediction (1.19) proved to be correct in the range of 5 eV above the threshold energy [4].

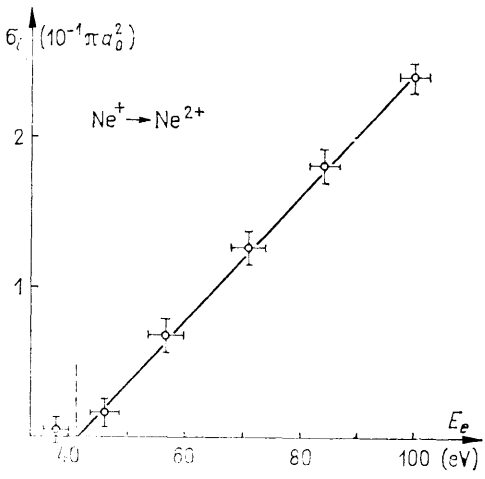

Fig. 1.20 Variation of ionization cross section values of Ne^+ ions with impact electron energies near the threshold energy

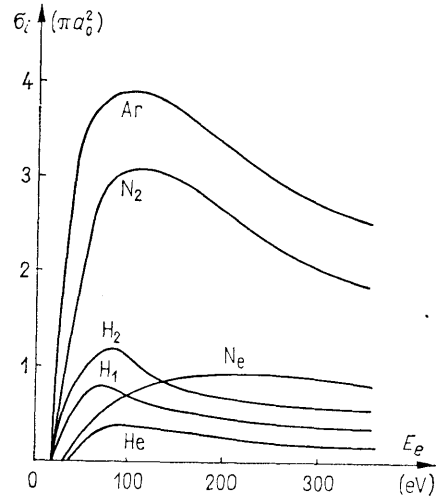

Fig. 1.21 Variation of the ionization cross section values of H_1, H_2, He, Ne, N_2 and Ar with impact electron energies

For the double ionization of sodium atoms the quadratic, for their triple ionization the cubic dependence was shown in an energy range of ~40 eV above the threshold energies for double and triple ionizations, respectively [76].

The validity of formula (1.19) was also confirmed by measurements on the ionization of noble gas atoms and ions [72–75, 77–80]. The ionization cross sections against impact electron energies, as measured at values close to the ionization threshold energies are shown for neon, argon and xenon in Figs 1.19 and 1.20.

The ionization function increases with increasing impact energies up to a maximum after which it decreases with increasing energies as shown for some molecules and atoms in Fig. 1.21.

For the evaluation of ionization cross sections both classical and quantum mechanical approximations or semi-empirical formulae can be used.

In the classical approach the inelastic collision leading to ionization can be treated as a collision of a pair of particles if the interaction between the striking and atomic orbital electrons only is considered. If in this case the motion of the atomic electrons is ignored, that is, the atomic electron is considered to be at rest at the time of the impact, then the energy imparted to the bound electron by the striking free electron is given by [94]

$$E = \frac{4m_1m_2}{(m_1+m_2)^2} \frac{E_{e_2}}{1+\dfrac{\varrho^2 v_{e_2}^4}{e_1e_2}\left(\dfrac{m_1m_2}{m_1+m_2}\right)^2} \tag{1.20}$$

where m_1, m_2; e_1, e_2; v_1, v_2; E_{e_1}, E_{e_2} stand for the masses, charges, velocities and energies of the free and bound electrons, respectively. For electron–electron collisions we have $e_1 = e_2 = e$ and $m_1 = m_2 = m$ and therefore formula (1.20) reduces to the Thomson expression [10] of the form

$$E = \frac{E_{e_2}}{1+\dfrac{\varrho^2}{e^4}E_{e_2}^2} \tag{1.21}$$

Hence the collision parameter ϱ can be obtained as

$$\varrho^2 = \frac{e^4}{(E^i)^2}\left[\frac{E}{E_{e_2}} - \left(\frac{E}{E_{e_2}}\right)^2\right] = \frac{e^4}{(E^i)^2} f\left(\frac{E}{E_{e_2}}\right) \tag{1.22}$$

Assuming that each transfer of energy $E > E^i$ leads to ionization, i.e. to a transfer of energy higher than E^i, then the cross section for collisions leading to ionization can be expressed for a number N of electrons in the outer shell of the atom to be ionized [10] as

$$\sigma_i = N\pi\varrho^2 = N\pi \frac{e^4}{(E^i)^2} f\left(\frac{E}{E_{e_2}}\right) \tag{1.23}$$

The Thomson formula (1.23) generally gives a qualitatively correct picture of the energy behaviour of the ionization cross section but the position

and value of the maximum do not agree well with the experimental data. It is apparent from Fig. 1.22 that the maximum value of the cross section was observed at higher energies than the Thomson prediction. It follows that the values calculated from (1.23) are overestimated at lower and underestimated at higher electron energies, by comparison with the experimental values.

In a further refinement of the classical model the motion of the atomic electrons is also taken into account [11, 13–15, 96]. In this formulation the experimental values are more comparable.

The best agreement with experiment is obtained from the classical two-particle collision model formulated by Gryzinski [11]. The ionization cross section for the transfer of impact energy $E > E^i$ is expressed in Gryzinski's formulation as

$$\sigma_i = \frac{\sigma_0}{(E^i)^2} f_1\left(\frac{E_{e_2}}{E^i}, \frac{E_{e_1}}{E^i}\right) \qquad [\mathrm{cm}^2] \tag{1.24}$$

where

$$f_1 = \left(\frac{E_{e_2}^2}{E_{e_2}^2 + E_{e_1}^2}\right)^{3/2} \begin{cases} \dfrac{2}{3}\dfrac{E_{e_1}}{E_{e_2}} + \dfrac{E^i}{E_{e_2}}\left(1 - \dfrac{E_{e_1}}{E_{e_2}}\right) - \left(\dfrac{E^i}{E_{e_2}}\right)^2 & \text{if } E^i \leq E_{e_2} - E_{e_1} \\ \dfrac{2}{3}\left[\dfrac{E_{e_1}}{E_{e_2}} + \dfrac{E^i}{E_{e_2}}\left(1 - \dfrac{E_{e_1}}{E_{e_2}}\right) - \right. \\ \left. - \left(\dfrac{E^i}{E_{e_2}}\right)^2\right]\left[\left(1 + \dfrac{E^i}{E_{e_1}}\right)\left(1 - \dfrac{E^i}{E_{e_2}}\right)\right] & \text{if } E^i \geq E_{e_2} - E_{e_1} \end{cases}$$

and

$$\sigma_0 = \frac{m_2}{m_1}(Z_1 Z_2)^2\, 6.56 \cdot 10^{-14} \qquad (\mathrm{eV})^2\ \mathrm{cm}^2$$

where E^i is given in electron volts and Z_i is the charge of the colliding particle in electron charge units.

In the case of an electron–electron collision, when $m_1 = m_2 = m$ and $Z_1 = Z_2 = Z$ and assuming that $E_{e_1} \approx E^i$, which strictly holds only in the ground state of hydrogen atoms, formula (1.24) reduces to

$$\sigma_i = 6.56 \cdot 10^{-14} \frac{Z^4}{(E^i)^2} f_2\left(\frac{E_{e_2}}{E^i}\right) \tag{1.25}$$

where

$$f_2 = \left(\frac{E_{e_2}^2}{E_{e_2}^2 + E_{e_1}^2}\right)^{3/2} \begin{cases} \dfrac{E^i}{E_{e_2}}\left(\dfrac{5}{3} - \dfrac{2E^i}{E_{e_2}}\right) & \text{if } 2E^i \leq E_{e_2} \\ \dfrac{2}{3}\dfrac{E^i}{E_{e_2}}\left(2 - \dfrac{2E^i}{E_{e_2}}\right)^{3/2} & \text{if } 2E^i \geq E_{e_2} \end{cases}$$

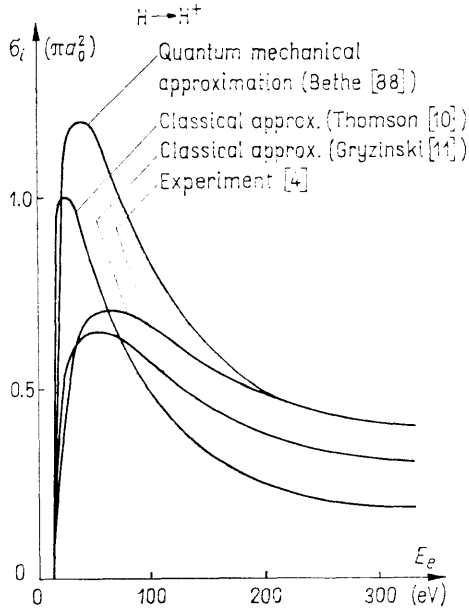

Fig. 1.22 Comparison of ionization cross section values obtained from experiment as calculated from different theories

It should be noted, however, that the limitation of the two-particle collision model is apparent even in these refined forms at higher impact energies where neither (1.24) nor (1.25) gives a satisfactory agreement with measured values (see Fig. 1.22). The reason for this is that the interaction during the time of collision between the striking electron and the residual atom is not accounted for in this model.

A wholly reliable result would be obtainable by accurate quantum mechanical calculations, but, as has already been mentioned, these are too difficult to perform.

At higher impact electron energies it is preferable to apply the Born approximation which permits the ionization cross sections to be predicted in good agreement with the experimental data [88–91]. However, at lower electron energies the predictions from the Born approximation are higher than the measured cross section values.

The deviation at the low energy end can be reduced to some extent by taking account of the exchange interaction [2, 31, 33, 70, 92] or by the distorted wave approximation [97, 98].

The Born approximation to the ionization cross section was formulated by Bethe for higher impact electron energies in the form [88]

$$\sigma_{nl}^{i} = \frac{2\pi e^4}{m_e v_e^2} \frac{C_{nl}}{|E_{nl}^{i}|} Z_{nl} \ln \frac{2m_e v_e^2}{O_{nl}} \tag{1.26}$$

where

$$C_{nl} = \frac{Z_{\text{eff}}^2}{n^2 a^2} \int | X_{nl,k} |^2 \, dk$$

Z_{nl} is here the number of electrons on the shell nl, the value of the parameter O_{nl} varies from 0.05 to 0.3, but can generally be approximated by 0.1. Z_{eff} is the effective charge of the nucleus the field of which acts on the shell nl of the electron, $X_{nl,k}$ is the matrix element proportional to the oscillator strength of the electric dipole transition.

The value of C_{nl} has been calculated for hydrogen atoms with respect to different nl shells [88] as

$1s$	$2s$	$2p$	$3s$	$3p$	$3d$	$4s$	$4p$	$4d$	$4f$
0.28	0.21	0.13	0.17	0.14	0.07	0.15	0.13	0.09	0.04

If hydrogen atoms are ionized from the ground state, (1.26) can be written in the form

$$\sigma_{1s}^i = 0.285 \frac{2\pi e^4}{| E_{1s}^i | \, m_e v_e^2} \ln \frac{2 m_e v_e^2}{0.48 \, | E_{1s}^i |} \tag{1.27}$$

The ionization function predicted from (1.27) agrees well with the experimental values in the energy range $E_e > 200$ eV, at lower energies the formula does not hold (see Fig. 1.22).

In order to improve the quantum mechanical approximation at lower impact energies a term arising from exchange interaction was introduced into the Born approximation [33]. The thus predicted values showed a better agreement with the experimental data on hydrogen atoms (Fig. 1.23).

As has been seen, the classical model describes the ionization function reasonably well at low impact energies and fails at high energies while the quantum mechanical approximation ceases to hold at low energies. Thus, attempts have been made to extend the validity of the classical model to higher energies by introducing different coefficients [12, 13, 81, 84, 86, 99], or to extend that of the quantum mechanical formalism to the low energy end [15, 82, 83, 93].

Among these attempts the semi-empirical formulae of the classical approach, which include a logarithmic term, have proved to be the most satisfactory. These formulae are a combination of the properties favourable in the classical formulae at lower energies with those of the Born approximation advantageous at higher energies.

For ionization by electron impact one of the two most satisfactory formulae was proposed by Gryzinski [12] as

$$\sigma_i = \frac{\sigma_0}{(E^i)^2} f_3 \left(\frac{E_{e_2}}{E^i} \right) \tag{1.28}$$

where in the case of electron–electron collision $\sigma_0 = 6.56 \cdot 10^{-14} Z_e^2 \, (\text{eV})^2 \, \text{cm}^2$

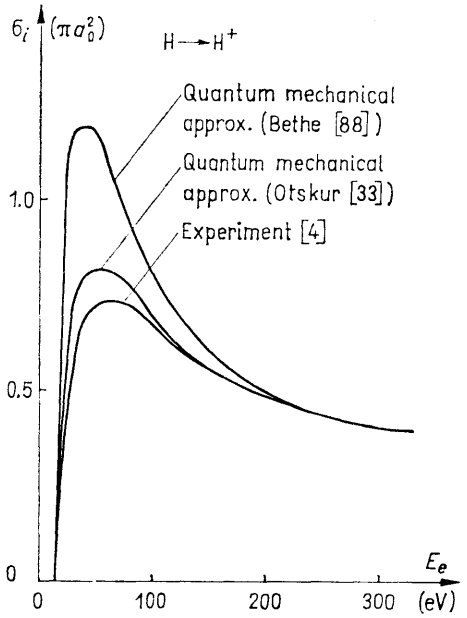

Fig. 1.23 Comparison of experimental ionization cross section values as calculated from the Born approximation formula (1.27) and from the expression accounting for exchange interaction

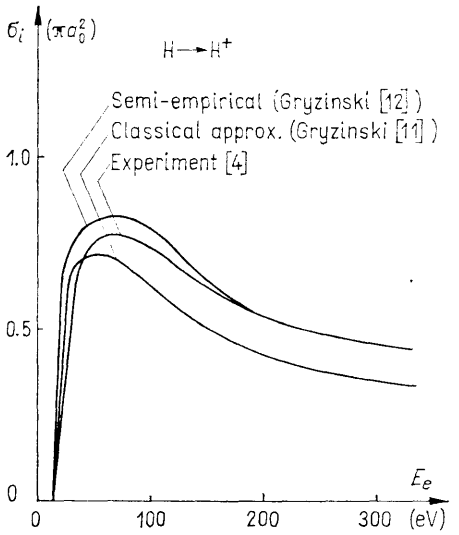

Fig. 1.24 Comparison of ionization cross section values of hydrogen atoms obtained from experiment as calculated from the classical approximation and from the semi-empirical formula

if E^i is given in eV units and

$$f_3 = \frac{E^i}{E_{e_2}} \left(\frac{E_{e_2} - E^i}{E_{e_2} + E^i} \right)^{3/2} \left[1 + \frac{2}{3} \left(1 - \frac{E^i}{2E_{e_2}} \right) \ln \left(2.7 + \sqrt{\frac{E^i}{E_{e_2}} - 1} \right) \right]$$

The other expression, proposed by Drawin [86], reads

$$\sigma_i = 2.66 \frac{\pi e^4 Z_n}{(E^i)^2} f_a \frac{E^i (E_{e_2} - E^i)}{E_{e_2}} \ln 1.25 f_b \frac{E_{e_2}}{E^i} \tag{1.29}$$

where $f_a = 0.7, \ldots, 1.3$; $f_b = 0.8, \ldots, 3.0$ which can generally be approximated by $f_a = 1.0$ and $f_b = 1.0$.

The cross section values calculated from expression (1.28) show a better agreement with the experimental data than those predicted from (1.24) or (1.25) (see Fig. 1.24).

The logarithmic correction in (1.29) reduces the value of the cross section to compare with that obtained from the Thomson formula at low energies, the maximum is smoothed by this term and the formula transforms at higher energies to that derived from the quantum mechanical approximation.

In Figs 1.25–1.28 the calculations from (1.28) and (1.29) are compared with the experimental values.

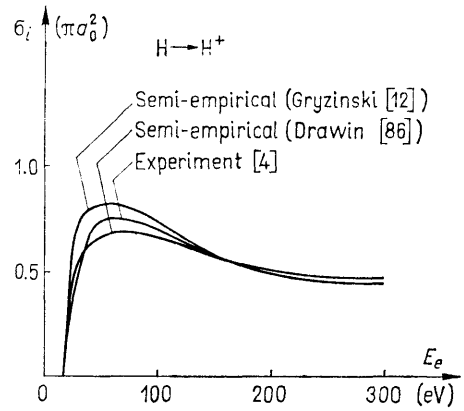

Fig. 1.25 Comparison of ionization cross section values as calculated from Gryzinski's and Drawin's semi-empirical formulae for hydrogen atoms with the experimental values

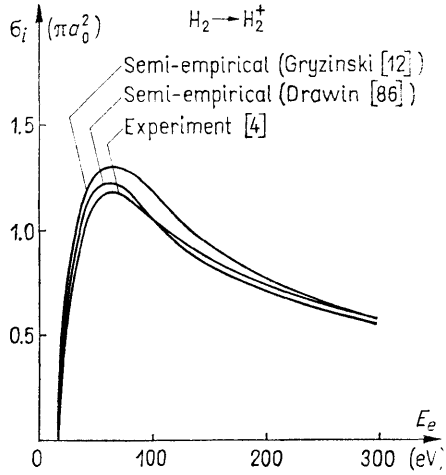

Fig. 1.26 Comparison of ionization cross section values as calculated from Gryzinski's and Drawin's semi-empirical formulae for hydrogen molecules with the experimental values

It is apparent from the figures that both expressions yield values in reasonably good agreement with the experimental data. Thus, both formulae can be used for the calculation of the ionization cross section when the error of the results involved in these relatively simple expressions is permissible in the given application.

If atoms are ionized from their excited states, the threshold energies for ionization are lower than required for ionization from their ground state

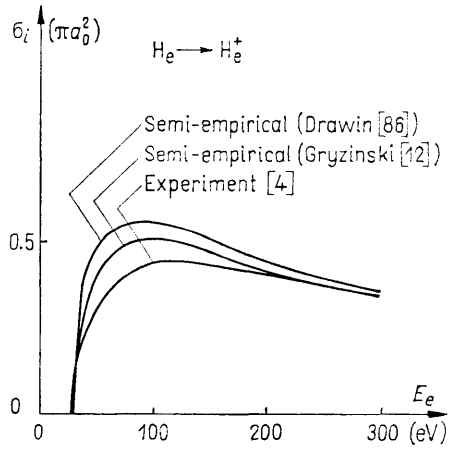

Fig. 1.27 Comparison of the ionization cross section values as calculated from Gryzinski's and Drawin's semi-empirical formulae for helium atoms with the experimental values

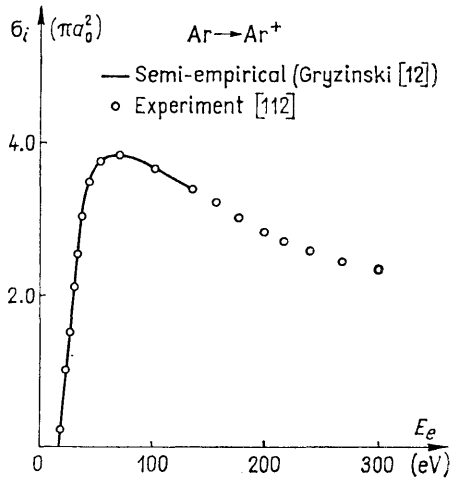

Fig. 1.28 Comparison of ionization cross section values as calculated from Gryzinski's semi-empirical formula for argon atoms with the experimental values

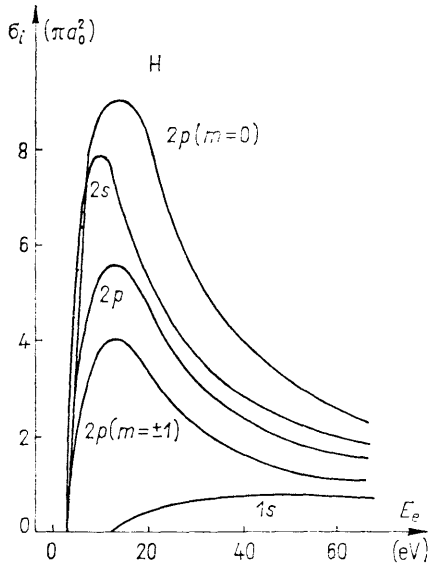

Fig. 1.29 Ionization cross section values as calculated from the Born approximation [107] for hydrogen atoms in the 1*s* ground state and in the 2*s*, 2*p* excited states

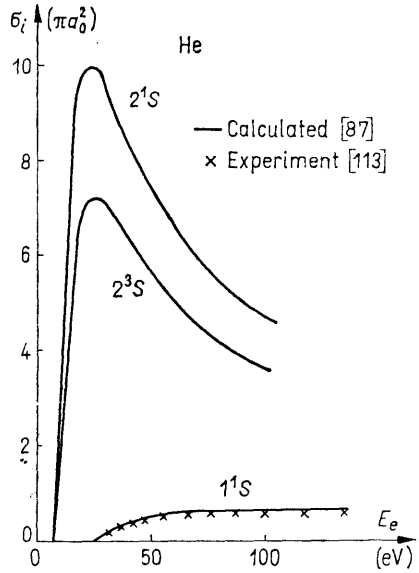

Fig. 1.30 Ionization cross section values as calculated from Gryzinski's semi-empirical formula for helium atoms in the 1^1S ground state and in the 2^1S and 2^3S excited states. Values calculated for the 1^1S state are compared with the experimental data

because the binding energies of the electrons are lower in the excited than in the ground state.

The ionization cross section values of excited atoms can be calculated from the formulae obtained by the classical and quantum mechanical approximations and the semi-empirical method for ionization from the ground state.

Both the calculated and the measured values [24, 107–110] indicate that the ionization cross sections of excited atoms are larger than those of atoms in the ground state.

This fact can be interpreted also in terms of the Bohr model. If the ionization cross section is considered to be delimited by the orbit of the electron assigned to the main quantum number n of the atom, then the ionization cross section of the atom in an excited state will be n^4/Z^2 times that of the ground state assigned to $n = 1$ since the radius of the Bohr orbit is given by

$$a_n = \frac{\hbar}{m_e e^2} \frac{n^2}{Z}$$

The ionization cross sections calculated from the quantum mechanical Born approximation for the $n = 1$ and $n = 2$ levels of hydrogen atoms [107] are shown in Fig. 1.29.

Ionization cross sections have also been predicted by the use of the Gryzinski formula (1.28) for the ground states and some excited levels of helium, neon, argon and mercury atoms [24]. The results for helium can be seen in Fig. 1.30.

These calculations and the conclusions of other workers who studied this problem [108–110] show steeper slopes and a shift of maxima towards lower impact energies in the ionization functions at excited levels as compared with those observed at ground states. Consequently, there is a considerable difference between the ionization cross section values for the excited and ground states. Multiple ionization can be brought about by electron impact on atoms either by a single impact on an atom in the neutral state, or by inducing gradually a transition from the (n)-th ionization state to the $(n + 1)$-th state.

The threshold energy for multiple ionization by single impact, symbolized by E_n^i, increases as the degree of ionization, n, increases (Appendix, Table 4), whereas the cross section for multiple ionization substantially decreases as the degree of ionization increases. This can be seen from Fig. 1.31 and Appendix, Table 5 [103, 111, 112, 118].

The maximum cross section value for multiple ionization can be predicted to an accuracy within an order of magnitude if the value of the ionization cross section in the state $n = 1$ is known. One can then use the empirical formula [119]

$$\sigma_n^i = \sigma_1^i \exp\left(-\frac{6.78}{A^{1/4}}\sqrt{n-1}\right) \tag{1.30}$$

where A is the atomic number.

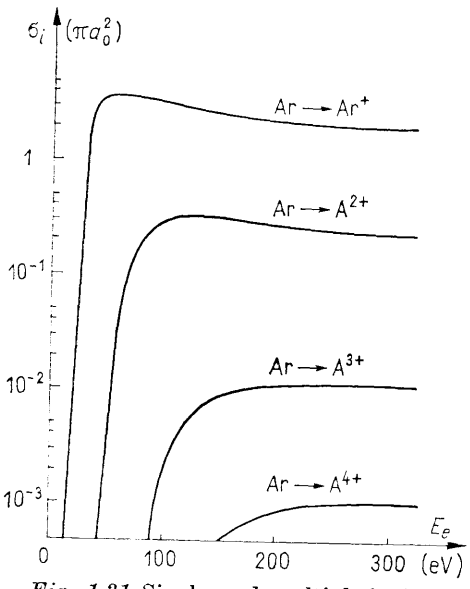

Fig. 1.31 Single and multiple ionization cross section values calculated for argon atoms

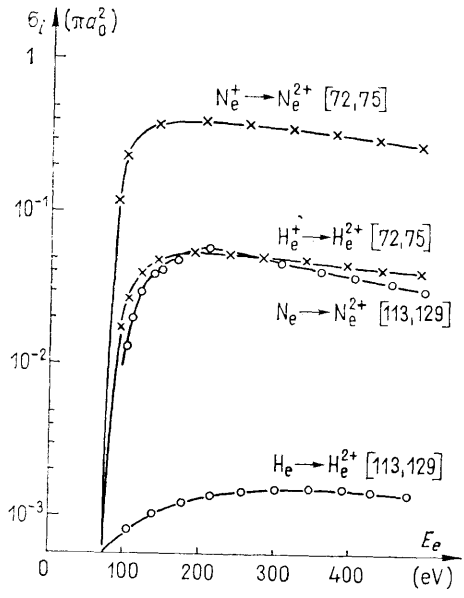

Fig. 1.32 Ionization cross section values calculated for helium and neon atoms and molecules

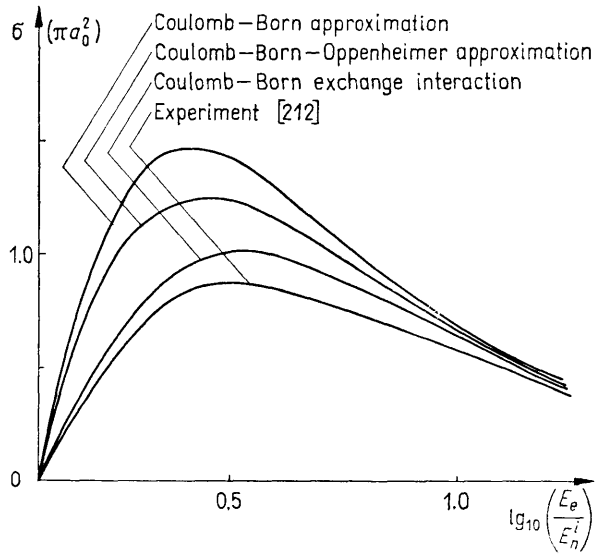

Fig. 1.33 Comparison of ionization cross section values of ions as calculated from different approximations taking into account the Coulomb field with values obtained from experiment

The maximum cross section values for multiple ionization calculated from (1.30) are compared with the measured values [103, 111, 112, 118] in Table 5. The alternative process, i.e. gradual ionization, can occur only if the lifetime of the n times ionized state is longer than the time interval between the inelastic ionizing collisions. The cross section for electron impact-induced transition from the n times ionized to the $n+1$ times ionized state is generally larger than that from the neutral to the $n+1$ times ionized state by a single impact [87, 91, 102, 111–113, 118, 120, 121]. Figure 1.32 shows the cross section values for the $He \rightarrow He^{2+}$, $He^{+} \rightarrow He^{2+}$, $Ne \rightarrow Ne^{2+}$ and $Ne^{+} \rightarrow Ne^{2+}$ transitions.

The ionization of positive ions differs from that of neutral atoms because the Coulomb field of the n times ionized atom affects the interaction due to the attractive force acting on the striking electron.

The ionization cross sections of ions can be evaluated to the best agreement with experimental data by the quantum mechanical method in terms of the Coulomb–Born approximation which also accounts for the exchange interaction [120, 212] (Fig. 1.33).

Reasonable agreement with experimental data has also been obtained for the ionization cross sections of ions predicted from the semi-empirical formula (1.28) [87], as is apparent from the comparison of the measured and calculated values for $He^{+} \rightarrow He^{2+}$ and $Ne^{+} \rightarrow Ne^{2+}$ processes in Fig. 1.34.

If atoms with higher mass number are struck by electrons, ionization can take place by electron ejection from the outer or inner electron shell of the atom. At low impact energies only the outer shell can be stripped of its electron whereas at higher energies either process can take place. The

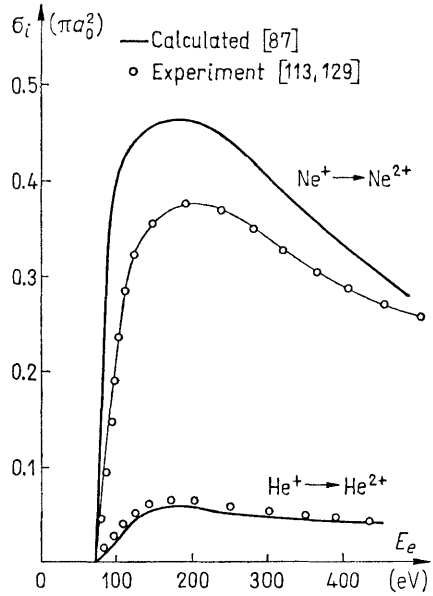

Fig. 1.34 Ionization cross section values as calculated from Gryzinski's semi-empirical formula for He^+ and Ne^+ ions as compared with experimental values

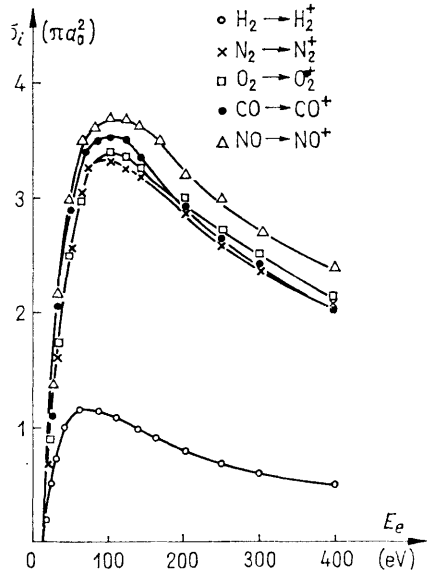

Fig. 1.35 Ionization cross section values for H_2, N_2, O_2, CO and NO molecules obtained from experimental data [103, 126–131]

electron ejection probability is much lower for the inner than for the outer shell. If the ionization occurs by electron ejection from the inner shell, the ejected electron is replaced by one from the outer shell and the excess energy of the latter is emitted in the form of radiation.

The calculation of the ionization of atoms with several electrons is rather complicated. It is difficult to compare the theoretical values with experimental data since the ionization from the inner shell has to be considered in addition to the simple process occurring from the outer shell, moreover, for atomic systems with several electrons the frequently occurring autoionization cannot be left out of consideration.

Calculations can therefore be performed above all for heavy atoms with a single valence electron which can be treated similarly to the ionization of hydrogen atoms, since the non-valence electrons form a closed shell and the valence electron can be regarded as a particle moving in the central field of the nucleus [91, 122, 125].

The ionization of molecules by electron impact occurs, similarly to excitation, according to the Frank–Condon principle. The threshold energy for ionization varies with the molecular state and corresponds to the difference between the energies of the potential energy curves for the transition from one electron state to another.

In the case of molecules the ionization process can be approached by considering the potential energy curves for the electron state of the molecule and the Frank–Condon principle.

The ionization cross sections of molecules have been studied by a number of authors [103, 126–131]. The results of measurements on hydrogen, nitrogen, oxygen, carbon monoxide and nitric oxide molecules are shown in Fig. 1.35.

1.2.2 IONIZATION OF ATOMS OR MOLECULES BY ATOM OR ION IMPACT

The ionization of atoms or molecules due to inelastic collision with atomic particles depends, similarly to excitation, on the states of the colliding particles and on the impact energy and it can occur in several ways.

The inelastic collision between atomic particles can lead to ionization if the impact energy is higher than

$$E_u = \frac{E_0^i(m_1 + m_2)}{m_2}$$

where m_1 and m_2 are the masses of the colliding particles [133, 134]. It follows from this expression that for $m_1 = m_2$, we have $E_u = 2E_0^i$, that is in the processes $H + H$ or $H^+ + H_1$ the impact energy must exceed by at least twice the value of the ionization potential to induce ionization.

At lower impact energies ionization can take place only if the colliding atoms or molecules are in an excited state and the excitation energy of one particle is transferred to the other during the inelastic collision. This process may happen in various ways, such as

$$A^* + B^* \rightarrow \begin{matrix} A^+ + B + e \\ A + B^+ + e \end{matrix} \tag{1.31}$$

$$A + B \rightarrow A + B^+ + e \tag{1.32}$$

In the reaction of type (1.31) the excitation energies of both atoms are imparted to one of the particles and the combined energies are sufficient for ionization.

The process of type (1.32) can occur only if the ionization potential E_B^i of particle B is lower than the excitation energy E_A^e of particle A, that is,

$$E_B^i < E_A^e$$

These processes are of particular importance if the excited atoms are in a metastable state. If the excited state of the A atom is metastable in the reaction (1.32), the process is usually known by the name 'Penning effect'. Appendix, Table 6 lists the processes of type (1.32) observed by different authors [136–141] together with the reported values of the cross sections.

Besides the reactions described by (1.31) and (1.32), ionization can take place at much lower energies than defined above if one of the colliding atoms is in an autoionized and the other in the ground state. In this case the autoionized state decays, during or after the collision, to an ion and an electron. The energy spectrum of the electrons released in the ionization process contains a set of resonances which correspond to the decays of the autoionized atomic states. This permits the autoionized states to be studied

by observation of the released electron spectrum. Thus, a number of autoionized states were identified in helium and argon atoms from the resonances in the electron spectrum [201–204].

Theoretically, this process can be interpreted in terms of the 'quasi-molecule' formed by the colliding particles [205–206], in the act of collision, when the basic term of the quasi-molecule is crossed by the boundary of the continuous spectrum. This can be followed by the decay of the quasi-molecule and the emission of a free electron. If the basic term of the quasi-molecules is crossed by the terms of the autoionization state of one of the colliding atoms, the collision process can lead to ionization.

Similarly to the energy dependence of the cross section for excitation, the energy curve for the ionization cross section on atom or ion impact exhibits a maximum. The ionization functions measured for some atoms and molecules can be seen in Fig. 1.36.

In the case of ion–atom collision the ionization cross section can be evaluated in terms of the quantum mechanical approximation by use of the Bethe formula

$$\sigma^i_{nl} = \frac{2\pi Z_i^2 e^4}{m_e v_i^2} \frac{C_{nl}}{|E^i_{nl}|} Z_{nl} \ln \frac{2m_e v_e^2}{O_{nl}} \tag{1.33}$$

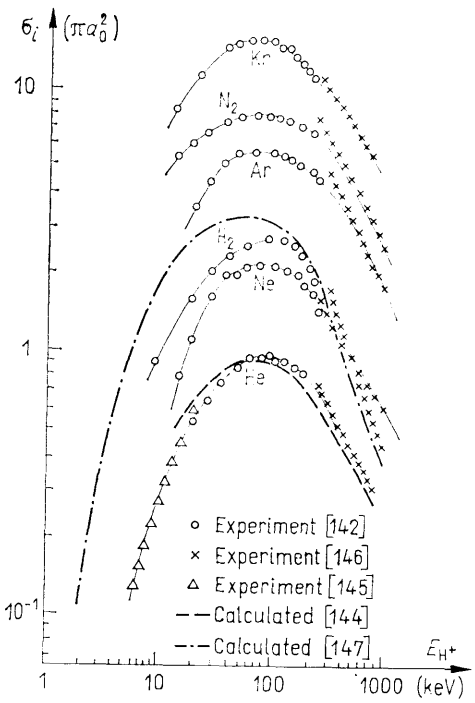

Fig. 1.36 Comparison of calculated and experimental ionization cross section values for He, Ne, Ar, Kr atoms and H_2, N_2 molecules on collision with H_1^+ ions

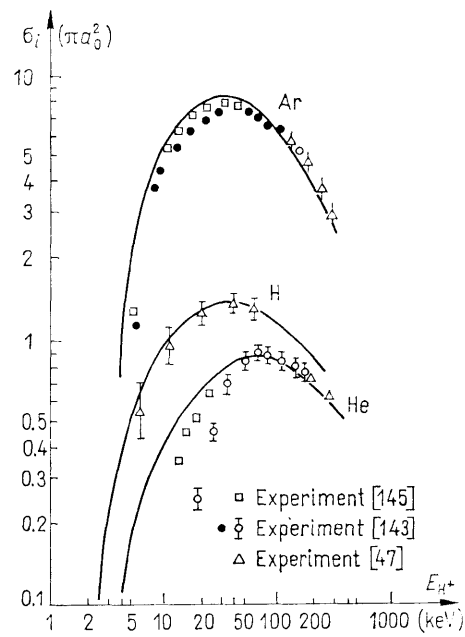

Fig. 1.37 Comparison of ionization cross section values as calculated from Gryzinski's formula (1.34) with the measured values for hydrogen, helium and argon atoms

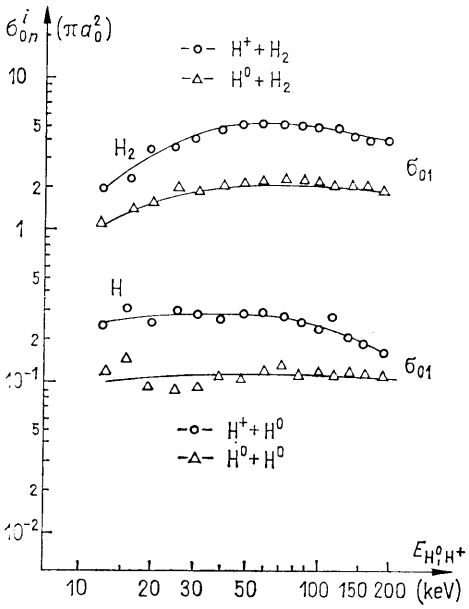

Fig. 1.38 Cross section values for single ionization measured on hydrogen atoms and hydrogen molecules bombarded with hydrogen atoms or hydrogen ions

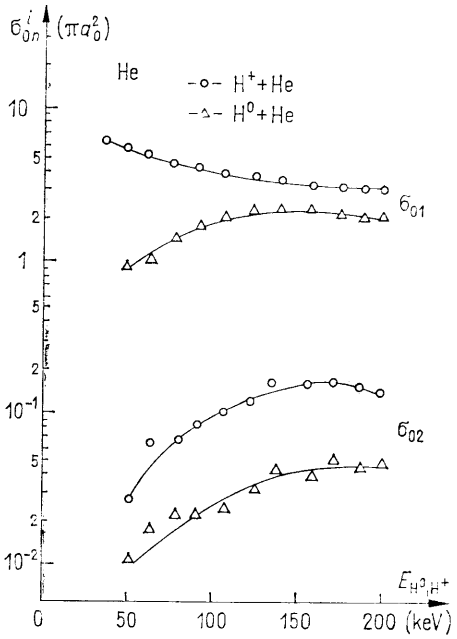

Fig. 1.39 Measured values of single and double ionization cross sections of helium atoms for collisions with hydrogen atoms or hydrogen ions

where Z_i is the charge of the colliding particles, while the other symbols are the same as those used in (1.26).

A good agreement with experimental data can also be obtained from the expression proposed by Gryzinski [12] as

$$\sigma_i = \frac{\sigma_0}{(E^i)^2} f_4 \left(\frac{v_r}{v}\right) \tag{1.34}$$

where

$$f_4 = \frac{v_r}{v} \left\{ \left(\frac{v_r}{v}\right)^2 \left(\frac{v_r^2}{v_r^2 + v^2}\right)^{3/2} \left[\frac{v_r^2}{v_r^2 + v^2} + \frac{2}{3}\left(1 + \frac{1}{\beta}\right) \ln\left(2.7 + \frac{v_r}{v}\right)\right] \cdot \right.$$
$$\left. \cdot \left(1 - \frac{1}{\beta}\right)\left[1 - \left(\frac{1}{\beta}\right)^{\left(1 + \frac{v_r}{v}\right)^2}\right]\right\}$$

with

$$\beta = 4\left(\frac{v_r}{v}\right)^2 \left(1 + \frac{v}{v_r}\right)$$

and v_r is the velocity of the bombarding particle.

The values predicted from (1.34) are compared with the measured values in Fig. 1.37.

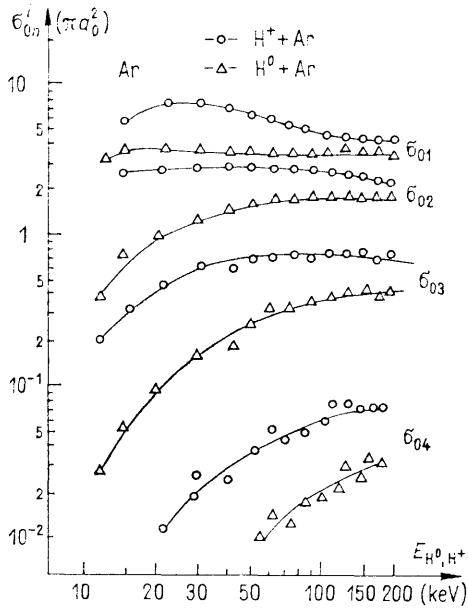

Fig. 1.40 Experimentally determined cross section values for single, double, triple or quadrupole ionization of argon atoms in collisions with hydrogen atoms or with hydrogen ions

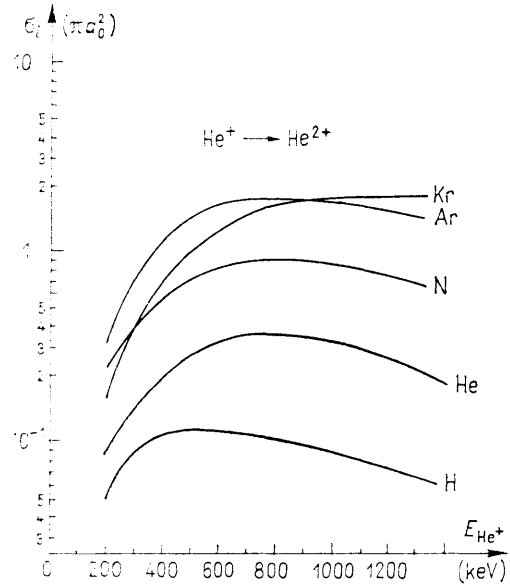

Fig. 1.41 Experimentally determined ionization cross section values of He^+ ions for collisions with hydrogen, helium, nitrogen, argon and krypton atoms

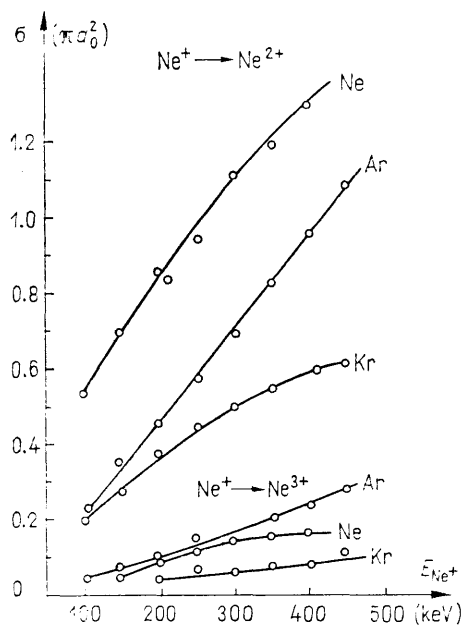

Fig. 1.42 Experimentally determined values of single or double ionization cross section of Ne^+ ions for collisions with argon, neon and krypton atoms

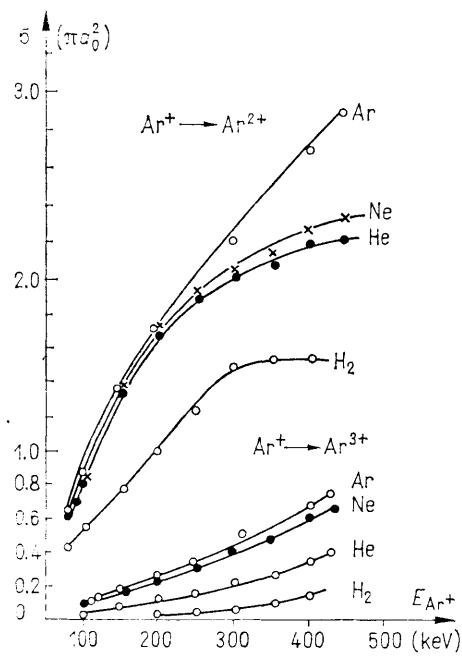

Fig. 1.43 Experimentally determined values of single or double ionization cross section of Ar^+ ions for collisions with hydrogen molecules and with helium, neon, or argon atoms

Numerous experiments and calculations have been made on the ionization cross sections of various gas atoms and molecules by H, H^+, He, He^+ or He^{2+} particles [142–149].

The measurements show that the ionization cross section values are higher for ion than for neutral atom impact and the maximum value exceeds in both cases that of the ionization cross section in the case of electron impact.

Figures 1.38–1.40 show the cross section values for single and multiple ionizations measured on hydrogen, deuterium, helium and argon bombarded with H^+ or H [142, 143]. The difference between the values obtainable by ion and neutral atom impact are easily apparent from the figure.

Figures 1.41–1.43 show the cross section values for the production of multiply charged ions, measured on hydrogen, helium, nitrogen, neon, argon and krypton gas bombarded with He^+, Ne^+ or Ar^+ ions [384, 385].

1.2.3 IONIZATION OF ATOMS AND IONS BY LIGHT QUANTA

Atoms and molecules can also be ionized upon the absorption of photons. This process is called photoeffect or photoionization. Ionization by photons differs from the excitation by light quanta in that the final state of the electrons taking part in the process lies in the continuous and not in the discrete energy spectrum.

Photoionization can occur if the energy $h\nu$ of the photon captured by the atom or molecule exceeds the ionization potential of the capturing particle, that is, if

$$h\nu > E^i_{nl}$$

Photons of any frequency which meet this requirement can be absorbed and thereby induce ionization. This means that the absorption spectrum is continuous in the case of photoionization.

The kinetic energy E^k_e of the electron released in photoionization is given by the Einstein equation

$$E^k_e = h\nu - E^i_{nl} \tag{1.35}$$

The photon energy $h\nu$ can be related to the length, through the equation

$$\mathrm{eV} = h\nu = h\frac{c}{\lambda}$$

hence

$$\lambda = \frac{hc}{\mathrm{eV}} = \frac{12\,400}{\mathrm{V}}\ \text{Å} \tag{1.36}$$

where V is to be understood in volt units.

The wavelengths corresponding to the ionization potential E^i_0 are listed for some atoms in Appendix, Table 3. It can be seen from the table that the ionization of gas atoms requires light quanta with fairly large energies and wavelengths lying in the ultraviolet or soft X-ray range of the wavelength spectrum.

The photoionization cross section, i.e. electron ejection by photons, can be evaluated for hydrogen atoms or for the K shell of ions analogous to hydrogen (with nuclear charge $Z \ll 137$) from the equation formulated from the known eigenfunctions of the continuous spectrum [150] as

$$\sigma_f^i = \sigma_T^i \frac{2^7 \pi \alpha^{-3}}{Z^2} \left(\frac{E_0^i}{h\nu}\right)^4 \frac{e^{-4\xi \operatorname{arc\,cot} \xi}}{1 - e^{-2\pi\xi}} \tag{1.37}$$

where

$$\sigma_T^i = \frac{2^2 \pi r_0^2}{3} = 6.65 \cdot 10^{-25}\ \mathrm{cm}^2 \tag{1.38}$$

is the scattering cross section for Thomson radiation with $r_0 = \dfrac{e^2}{mc^2} = 2.818 \cdot 10^{-13}$ cm, i.e. the classical electron radius, while $\alpha = \dfrac{1}{137} = \dfrac{e^2}{\hbar c}$ is the fine structure constant and

$$\xi = \sqrt{\frac{E_0^i}{E_e^k}} = \frac{Ze^2}{\hbar\nu}$$

In formula (1.37) it is assumed that the energy of the incident light quantum is high compared with the ionization energy of the electron on the K shell and that the energy of the outflying electron is low compared with its rest energy mc^2, that is,

$$E_0^i \ll h\nu \ll mc^2$$

which means that the relativistic correction is small.

Close to the ionization threshold, when $h\nu \to E_0^i$, that is, $\xi \to \infty$, formula (1.37) can be reduced to

$$\sigma_{f_0}^i = \sigma_T^i \frac{2^7 \pi\, 137^3}{(2.71)^4} \tag{1.39}$$

Now, if the condition $E_0^i \ll h\nu \ll mc^2$ is satisfied and the Born approximation can be applied $\left(\xi = \dfrac{Ze^2}{\hbar\nu} \ll 1\right)$, expression (1.37) takes the form

$$\sigma_{f_1}^i = \sigma_T^i \frac{2^6 \cdot 137^3}{Z^2} \left(\frac{E_0}{h\nu}\right)^{\frac{7}{2}} \tag{1.40}$$

The values calculated from the exact formula (1.37) and from the approximation (1.40) are compared in Fig. 1.44 with those determined from experiments [154, 155]. It can be seen that the values predicted by use of the exact formula (1.37) agree well with the experimental data.

It has to be noted, however, that at lower photon energies the photoionization cross section expressed exclusively for the K shell may include a contribution from photoionization on the outer shells which cannot be ignored.

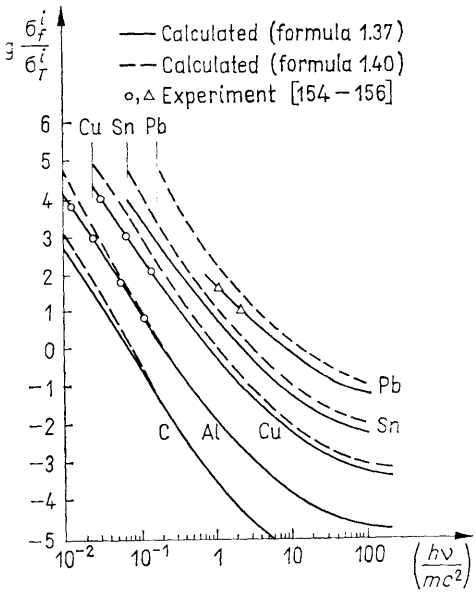

Fig. 1.44 Comparison of logarithmic values of the ratios of photoionization cross section σ_f calculated from the exact formula (1.37) or from the approximation formula (1.40) to the Thomson radiation cross section σ_T with measured experimental values

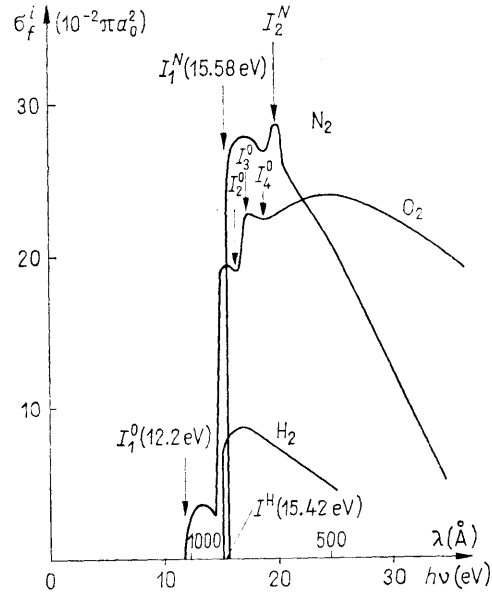

Fig. 1.45 Photoionization cross section values calculated for hydrogen, nitrogen and oxygen molecules by use of formula (1.42)

In the relativistic case, when the energy $h\nu$ of the incident quantum is much higher than the ionization potential, i.e.

$$E_0 \ll h\nu \geq mc^2$$

the photoionization cross section can be evaluated from the formula [151, 152]

$$\sigma_{f_2}^i = \sigma_T^i \frac{3Z^5\alpha^4}{2} \frac{(\gamma^2-1)^{3/2}}{(\gamma-1)^5} \cdot \left[\frac{4}{3} + \frac{\gamma(\gamma-2)}{\gamma+1}\left(1 - \frac{1}{2\gamma\sqrt{\gamma^2-1}} \ln \frac{\gamma-\sqrt{\gamma^2-1}}{\gamma+\sqrt{\gamma^2-1}}\right)\right] \tag{1.41}$$

where

$$\gamma = \frac{1}{\sqrt{1-\frac{v^2}{c^2}}}$$

If the system is analogous to hydrogen, the photoionization cross section is given for light atoms also by the function of the form [157, 158]

$$\sigma_f^i(\nu, n) = \frac{g2^5\pi e^6 Z^4 R}{3^{3/2}h^3\nu^3 n^5} \tag{1.42}$$

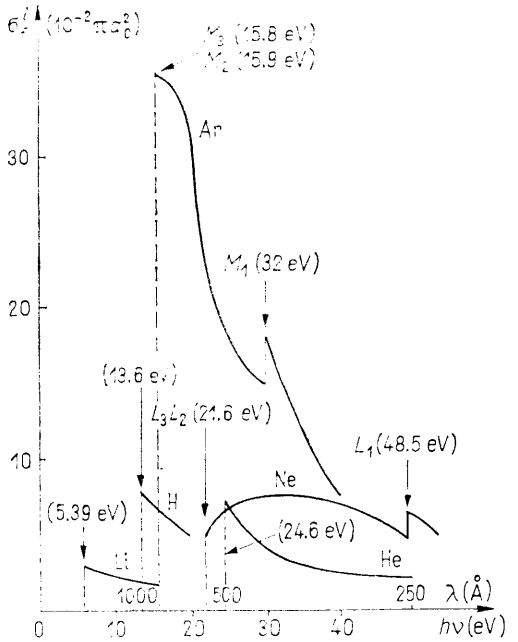

Fig. 1.46 Photoionization cross section values calculated for hydrogen, lithium, helium, neon and argon atoms by use of formula (1.42)

where $R = \dfrac{2\pi^2 e^4 m}{\hbar^2 c}$ is the Rydberg constant, n is the main quantum number of the initial state, and g is the multiplying factor evaluated in [158] which can generally be taken as $g = 1$ (the deviation from this value being not more than 10–20 per cent).

Photoionization cross section values calculated for given atoms and molecules from formula (1.42) are shown in Figs (1.45) and (1.46). The measured values obtained in numerous experimental studies of photoionization [160–173] show a good agreement with those calculated from (1.42).

1.2.4 AUTOIONIZATION

Autoionization takes place if two of the atomic electrons are simultaneously excited by impact or radiation with the sum of the two excitation energies being higher than that required for the ejection of one of these electrons.

The energy level corresponding to the autoionization state belongs to the continuous spectrum. The autoionization state may cease if one of the excited electrons is brought by the interaction between electrons to a lower level while the other is released and a positive ion is formed.

There are several ways in which autoionization states can be produced. One of them is autoionization initiated by two electrons excited to nearly the same degree, in another case the residual atom, in addition to one of

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Lecture Notes in Physics

Edited by J. Ehlers, München, K. Hepp, Zürich
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83

Experimental Methods in Heavy Ion Physics

29,-

Edited by K. Bethge

Springer-Verlag
Berlin Heidelberg New York 1978

2 Fundamental MCIS-Processes

2.1 Ion Production

Multiply charged ions can be produced by inelastic collisions between atoms, molecules or their ions on one side and photons, electrons or heavy particles on the other. As an example, in fig. 2.1 typical courses of the different cross sections are given, if photons, electrons and protons are chosen as projectiles, respectively.

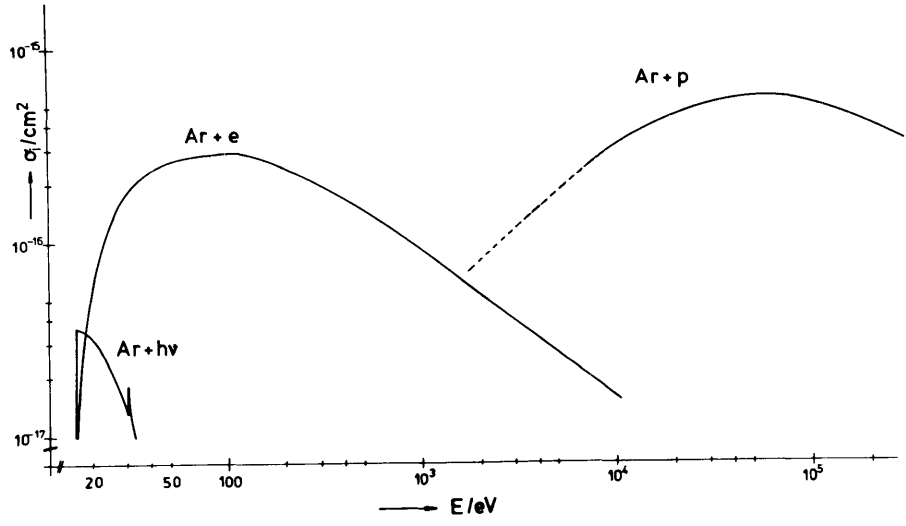

Fig. 2.1: Comparison of ionisation cross sections of Ar for photon, electron and proton impact, respectively.

In principle, photoionisation would be the best suited process since photons transfer only very little momentum to heavy particles; however, it must be ruled out as an efficient MCI-production process since the cross sections are rather small except near resonance energies, and furthermore, because intense sources of photons in the energy range above 5 eV are still not available.

Ionisation by heavy particle bombardment may take place with considerable cross sections; but the necessarily high particle velocities will also cause very high momentum transfer and thus will lead to unbearable MCI-energy spread; furthermore, the production of intense ion beams for these purposes would cause too much expenditure.

In contrary to the former processes electron collision leads to high cross sections even at low electron energy; the cross section maximum usually appears at a value of two to five times the respective ionisation potential. Much less momentum transfer to the target particles is achieved than with heavy projectiles; per collision the mean transferred energy amounts to

$$\Delta E = 2.E_e.\frac{m_e}{m_i}$$

The main reason for the choice of electrons as ionising particles follows from the convenient means of producing intense electron beams, e.g. in electrical discharges; hereby the importance of plasma ion sources can be seen.
The MCI-production can be accomplished by either one of the following processes:

a.) Outer shell ionisation
One or several electrons of the outermost atomic shell are removed by one single electron collision.
b.) Inner shell ionisation with subsequent rearrangement processes
Electrons with higher energy may also remove electrons from inner atomic shells; this can take place either by direct electron collisions or due to electronic shake off (CARLSON et al. 1968/1). In the latter case, the shell vacancy will be caused by a sudden perturbation due to the approaching projectile.
Ions with inner shell vacancies are highly excited systems; deexcitation takes place by recombining with electrons from outer shells; these transitions may be accompanied by radiation (emission of characteristic X-rays) or, in competition, the transitions may be radiationless ones (AUGER-transitions), where the excess energy causes the emission of one or more further electrons.
For atoms with $Z < 10$ the probability for a radiationless transition is almost 1; with increasing Z it decreases gradually; for K-shell vacancies at the heaviest particles values of almost 0, for L-shell vacancies values of about 0.5 and for outer shell vacancies values of more than 0.9 are typical (BURHOP 1952).
Following the recombination of an inner shell vacancy, outer shell vacancies can be created; thus, an inner shell vacancy may directly lead to multiple ionisation via AUGER-cascades.
A certain ion charge state z can be reached in the following ways:

a.) Single impact ionisation $X^{o} + e \rightarrow X^{z+} + (z+1)e$

b.) Stepwise ionisation
$$X^{o} + e \rightarrow X^{a+} + (a+1)e \qquad (a \geqslant 1);$$
$$X^{a+} + e \rightarrow X^{b+} + (b-a+1)e;\ldots.$$
$$X^{m+} + e \rightarrow X^{z+} + (z-m+1)e$$

If the ionisation steps are small (only outer shell processes), the respective cross sections for case b.) are usually considerably higher than for ionisation processes as specified in a.); with increasing CS the cross sections for single electron removal decrease much slower than the cross sections for single impact ionisation according to a.); therefore, it is advantageous to produce highly ionised atoms by stepwise ionisation processes if only the ions can be confined long enough in the ionisation region, so that the desired charge state can be approached.
Because experimental data on ionisation cross sections are quite scarce (KIEFFER and DUNN 1966; KIEFFER 1969; MASSEY and BURHOP 1969; HASTED 1972), especially for higher CS, calculations are needed. On the other hand, for atoms and ions with more than one electron the calculation of cross section is very difficult especially in the

region of the cross section maximum (MOTT and MASSEY 1965; RUDGE 1968).
Several authors (e.g. DRAWIN 1961; THOMAS and GARCIA 1969; LOTZ 1967 - 1970) have developed empirical expressions which are especially suited for the estimation of the cross section for removal of one single outer shell electron. Thereby the binding energies of all electrons in the outermost shell are needed; they can be deduced e.g. from the work of CARLSON et al. (1968/2).
The sequence of calculated ionisation potentials for removal of one outer shell electron for all Xe-ions is given in fig. 2.2; at the low CS, comparison is made with experimental values taken from REDHEAD (1967); furthermore, the appearance potentials for single impact ionisation into CS up to 10 have been deduced from CARLSON et al. (1968/2) and are plotted in fig. 2.3; comparisons are made with experimental values from DORMAN et al. (1959), FOX (1960) and STUBER (1965).

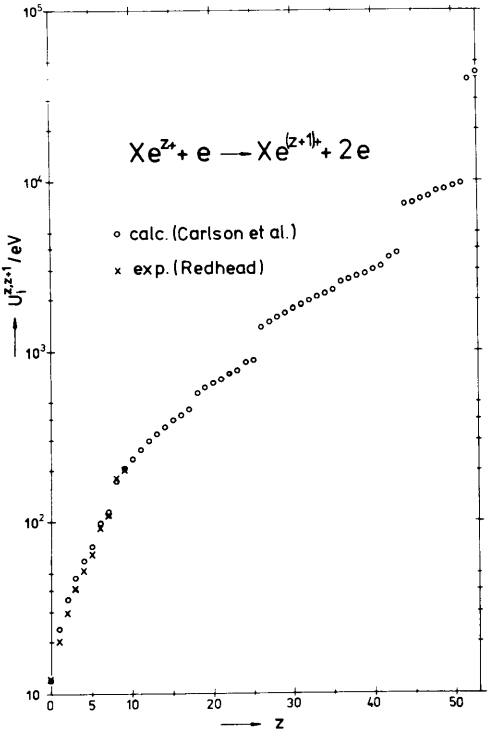

Fig. 2.2: Sequence of first ionisation potentials of Xe-ions

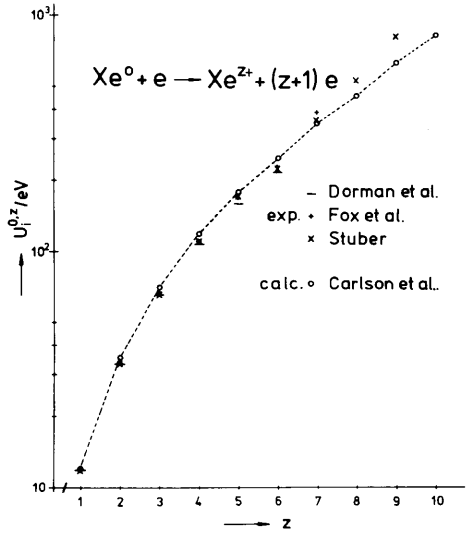

Fig. 2.3: Single impact ionisation potentials of Xe; comparison of calculated and measured data.

By inspection of fig. 2.3 it can be seen that with increasing CS considerable discrepancies arise between calculated and measured data; therefore, care must be taken if data are to be deduced from calculations, especially for higher CS.
A further, important parameter in such empirical formulae is the number of "equivalent" electrons in the atomic shell under consideration; thereby, electrons of inner shells must be considered, too, if they can be removed at the respective projectile energy.