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Experiments on Electron-Impact Excitation and Ionization of Ions*

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CONTENTS

	<u>Page</u>
1. INTRODUCTION	1
2. ELECTRON-IMPACT EXCITATION	3
2.1 <u>Fundamentals</u>	3
2.1.1 Threshold Behavior	3
2.1.2 High-Energy Behavior	4
2.1.3 Excitation and Emission Cross Sections	4
2.1.4 Polarization of the Radiation	5
2.1.5 Collision Strengths and Predictor Formulae	6
2.1.6 Detailed Theoretical Methods	7
2.2 <u>Colliding-Beams Experiments</u>	8
2.2.1 Hydrogen-Like Ions	9
2.2.2 Helium-Like Ions	10
2.2.3 Lithium-Like Ions	10
2.2.4 Sodium-Like Ions	13
2.2.5 Angular Differential Measurements	13
2.2.6 Other Ions	14
2.3 <u>Excitation Rate Coefficients from Plasmas</u>	15
2.4 <u>Other Methods</u>	17
3. ELECTRON-IMPACT IONIZATION	18
3.1 <u>Fundamentals</u>	18
3.1.1 Ionization Mechanisms	18
a. Direct Ionization	18
b. Ionization-Autoionization	18
c. Excitation-Autoionization	19
d. Resonant-Recombination Double Autoionization	20
3.1.2 Threshold Behavior	20
3.1.3 High-Energy Behavior	21
3.1.4 Predictor Formulae	22
a. The Lotz Formula	22
b. The Burgess-Chidichimo Formula	23
3.1.5 Theoretical Approaches	24
3.2 <u>Experimental Methods</u>	25
3.2.1 Intersecting-Beams Method	26
3.2.2 Plasma Spectroscopy Method	26
3.2.3 Trapped-Ion Method	27
3.3 <u>Experimental Results for Ionization</u>	27
3.3.1 Single Ionization	28
3.3.2 Multiple Ionization	30
3.4 <u>General Remarks about Electron-Impact Ionization of Ions</u>	32
REFERENCES	34

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1. INTRODUCTION

The challenge of understanding the characteristics and behavior of the so-called fourth state of matter, the ionized plasma, requires quantitative information on both the structure and collisional properties of ions. The simple glow-discharge tube, the laboratory ion source, the controlled-thermonuclear fusion plasma, the ionosphere, the solar corona — they all share one common attribute — their microscopic and macroscopic properties are controlled to a large degree by inelastic collisions between electrons and ions. The delicate balance produced by the continual interchange of kinetic, radiative and potential energy determines the signature by which such a plasma communicates with its surroundings, namely the light it produces. For even the simplest of plasmas, the interpretation of the spectrum of radiation which is emitted requires detailed knowledge of both the electronic structure of the ionic species present, and of the collision processes by which these ions reach and leave the excited ionic states from which the radiation occurs. At higher particle densities, the transport of radiation within the plasma must also be taken into consideration.

The quantitative study of inelastic collisions between electrons and ions has been motivated for many years by the astrophysical community. The need for accurate collision cross sections has been dramatically inten-

sified during the last decade by the worldwide emphasis on controlled-thermonuclear-fusion research, and its development as a potential energy source. The energetic radiation from highly ionized impurities in such high-temperature plasmas represents a serious mode of energy loss which has thus far prevented such devices from reaching the required ignition temperatures ($kT > 10 \text{ keV}$) and confinement times ($n\tau > 10^{14} \text{ cm}^{-3}\cdot\text{s}$). The effect of impurity ions on plasma confinement is also poorly understood, and may perhaps even be beneficial under certain circumstances [1]. Accurate models for plasmas require reliable cross section data for electron-impact excitation, ionization and recombination of these impurity ions.

Since the pioneering intersecting-beams experiments of Dolder, Harrison and Thonemann [2] in 1961 on electron-impact ionization, and of Dance, Harrison and Smith [3] on electron-impact excitation in 1966, considerable progress has been made in electron-ion collisions, particularly in the case of ionization. This careful early work set a high standard for research in the field, and it is interesting to note that despite significant refinements in such areas as detectors, optical calibration standards, data acquisition, computer control and ion sources, the basic technique of these experiments remains unaltered. Useful data have been produced by other techniques, such as monitoring spectral-line emission from magnetically confined plasmas [4], or by storing ions in a trap [5], but it is generally accepted that the colliding-beams method is capable of producing the most definitive basic data, since all the important parameters may be directly measured, and diagnostic checks performed. Such techniques form the subject of lectures to be presented at this meeting by P. Defrance, and will therefore not be addressed here, except for purposes of categorization

of experiments. Similarly, the theory of excitation and ionization of ions will be discussed in detail in the lectures of M. S. Pindzola and will not be addressed here per se.

The subjects of electron-impact excitation and ionization of ions have been thoroughly reviewed by D. H. Crandall [6] and E. Salzbom [7], respectively, at the preceding NATO Advanced Study Institute on this same topic, held at Baddeck, Canada, in 1981. Useful reviews have also been given at two other NATO Advanced Study Institutes on related themes by Dolder [8] on excitation and ionization of positive ions, and by Crandall [9] on collisions of electrons with multiply charged ions.

The present report will review some of the fundamental aspects, and then focus on highlighting some of the important experimental results which have been produced during the interim period.

2. ELECTRON-IMPACT EXCITATION

2.1 Fundamentals

2.1.1 Threshold Behavior

The cross section for excitation of an ion by a free electron has the distinct characteristic of being finite, and often having its maximum value, at the threshold energy for the process. This threshold corresponds to the difference in energy between the initial and final ionic states. This is in sharp contrast to that for excitation of a neutral atom, which rises from zero at threshold. The characteristic can only be accounted for quantum-mechanically and is a consequence of the Coulomb attraction between the electron and the ion. In this near-threshold region, resonances often

an important role in the excitation process, and must be taken into account in accurate theoretical predictions of the cross section. At asymptotically high energies, perturbation methods generally give an accurate account of the cross section. Thus, ion excitation by electrons is most important in the energy region where theory is most difficult and least reliable. Accurate experimental data are needed near threshold to benchmark the calculations.

2.1.2 High-Energy Behavior

At high collision energies (i.e., above about ten times the excitation threshold), the energy-dependence of the cross section is well-defined, and depends on the specific type of excitation process.

For dipole-allowed transitions ($\Delta l=1$, $\Delta s=0$), the cross section dependence on electron energy E follows the well-known Bethe form:

$$\sigma = \frac{A}{E} \ln(BE) \quad (A, B \text{ are constants}) \quad 2.1$$

For dipole-forbidden, spin-allowed transitions ($\Delta l \neq 1$, $\Delta s=0$), the cross section has the dependence:

$$\sigma = \frac{C}{E} \quad (C \text{ is a constant}) \quad 2.2$$

For dipole- and spin-forbidden transitions ($\Delta l \neq 1$, $\Delta s \neq 0$), the cross section falls off even more rapidly:

$$\sigma = \frac{D}{E^3} \quad (D \text{ is a constant}) \quad 2.3$$

2.1.3 Excitation and Emission Cross Sections

The signature of the excitation event is generally the emission of a photon as the excited level decays. If the excited level can only be popu-

lated directly by electron impact, a so-called level excitation cross section may be obtained from the photon emission as the ion radiatively decays. The branching ratio for emission of that wavelength and the polarization of the radiation must also in general be taken into account. If the branching ratio is unknown, or if the excited level may be populated by cascading from higher levels excited by electron impact, a photon emission cross section may be determined. It is possible for a given measured cross section to represent an excitation cross section at energies up to the threshold for the first cascading level, and an emission cross section thereafter. The general form of the energy dependence of a photon emission cross section may therefore be some combination of those given above:

$$\sigma = \frac{A}{E} \ln(BE) + \frac{C}{E} + \frac{D}{E^3} \quad 2.4$$

where A, B, C, and D are constants.

2.1.4 Polarization of the Radiation

In general, the emitted radiation will be polarized, and this must be considered in determining cross sections. Measurement of the polarization itself is independent of the absolute calibration of the photodetector, and provides a stringent test of theory, since it describes ratios of individual sublevel excitation cross sections. For dipole-allowed transitions, it has been shown that the constant "B" in the Bethe formula (2.1) can be determined from the energy E_0 at which the polarization passes through zero [10]. The constant B in Eq. 2.1 is given by $B = e^3/E_0$. The constant "A" in Eq. 2.1 can be calculated from the optical oscillator strength "f" for the transition, if it is known, and from the transition energy ΔE :

$$A = \frac{4\pi a_0^2 f}{\Delta E} \quad 2.6$$

where a_0 is the Bohr radius. Thus the absolute magnitude of the cross section at high energies may be determined in the Bethe approximation by measuring only the polarization of the emitted radiation. This provides an important consistency check for both experiment and theory.

2.1.5 Collision Strengths and Predictor Formulae

Theoretical calculations on electron-impact excitation are most commonly presented in terms of the so-called "collision strength", defined as follows:

$$\Omega = \omega \sigma E \quad 2.7$$

where ω is the statistical weight of the initial or lower level, equal to $(2S+1)(2L+1)$, or $(2J+1)$ if fine-structure is taken into account; E is the collision energy in Rydbergs; and σ is the cross section in units of πa_0^2 . This is the collisional analog of the oscillator strength for radiative transitions. For dipole-allowed transitions, a "Bethe plot" of the collision strength versus $\ln(E)$ becomes linear at high energies, the slope being proportional to the optical oscillator strength (see Eqs. 2.1 and 2.5).

Both astrophysicists and plasma physicists frequently use the well-known "g-bar" or "Gaunt-factor" formula of Seaton [11] and van Regemorter [12] to obtain estimates of excitation cross sections:

$$\sigma = \frac{8\pi}{\sqrt{3}} \cdot \frac{f}{E} \cdot \frac{\bar{g}}{\Delta E} \cdot \pi a_0^2 \quad 2.8$$

where E is the incident electron energy (in Rydbergs), ΔE is the transition energy (in Rydbergs), f is the optical oscillator strength for the tran-

sition, a_0 is the Bohr radius, and $\bar{g}$ is the "effective Gaunt factor". For singly charged ions, a value of $\bar{g}=0.2$ was found to reproduce experimental results reasonably near threshold, to well within the advertised factor of two. Crandall [6] and Younger and Wiese [13] have performed critical analyses of the values which have been recommended and used for $\bar{g}$ for multiply charged ions. For dipole-allowed $\Delta n=0$ transitions, a value near unity seems optimal. For $\Delta n \neq 0$ and dipole-forbidden transitions, the value ranges between 0.05 and 0.7, depending on the transition. Clearly, no simple formula will describe the excitation process to a high degree of accuracy for all ions, but it can be expected that Eq. 2.8 will probably be reliable to within a factor of two or so near threshold, provided that $\bar{g}$ is chosen as prescribed.

It should be noted that when the Gaunt-factor formula is used with a constant value for $\bar{g}$, it does not have the correct asymptotic (Bethe) energy dependence for dipole-allowed transitions (Eq. 2.1). In the original formulation, an energy-dependent prescription for $\bar{g}$ was given to take this into account [12]. At higher energies, the recommendation is:

$$\bar{g} = \frac{\sqrt{3}}{2\pi} \ln(E/\Delta E) \quad 2.9$$

The usual procedure is to use a constant value of $\bar{g}$ from threshold to the energy where Eq. 2.9 produces that value, and to use Eq. 2.9 for higher energies.

2.1.6 Detailed Theoretical Methods

A spectrum of theoretical procedures has been applied to electron-impact excitation of ions. Highly recommended for the experimentalist or nonspecialist is the introduction to theory presented by Crandall [6].

Further details may be found in reviews by Henry [14] and Robb [15], and in other papers and reviews cited therein. Since reference will be made to a number of theoretical methods in comparing to experiments, a few comments are in order. In approximately increasing order of sophistication, some of the methods which have been applied are:

Semiclassical Binary-Encounter Approximation

Plane-Wave Born Approximation

Glauber Approximation

Coulomb-Born Approximation

Coulomb-Distorted-Wave Approximation

Close-Coupling or R-Matrix Method.

The first three cannot account for the finite cross section at threshold for ion excitation by electron impact, but often give reasonable results at high energies. The last four have in specific cases each reproduced experiment very well, but have proven inadequate in others. The close-coupling or R-matrix method is in principle the most accurate, but may produce inferior results to the distorted-wave method, unless all important levels and couplings are explicitly taken into account. Allowance for other effects such as electron exchange, electron-electron correlations in the target wave functions, recombination resonances and unitarization can each be important in specific cases, and can rearrange the general hierarchy of approximations from that given above.

2.2 Colliding-Beams Experiments

Although theoretical calculations of ion excitation by electrons are numerous, the experiments are extremely sparse. All total cross section and rate-coefficient measurements reported to date have been based on the detection of photons radiated as the excited level decays. Photon disper-

sion, finite detection solid angle and detector efficiency all reduce signal count rates from intersecting-beam experiments to extremely low levels. Absolute optical calibration also becomes prohibitively difficult at the shorter wavelengths which are characteristic of the multiply-charged ions which are important in high-temperature plasmas. Useful data on excitation of ionic inner-shell electrons has also been obtained in crossed-beams experiments for electron-impact ionization, via the excitation-autoionization process.

2.2.1 Hydrogen-Like Ions

The first ion excitation to be studied by the crossed-beams method was the $1s-2s$ transition in the simplest one-electron ion, He^+ . Dance et al. [3] and Dolder and Peart [16] detected the 30.4 nm Ly- α radiation emitted when the $2s$ and $2p$ levels were Stark-mixed in an electric field. The independent experiments are consistent with each other, but when normalized to theory at high energy, the measured cross sections near the 41 eV threshold are only about half the best close-coupling estimates. This is especially confusing, since structure observed just above the threshold is well reproduced by theory.

Dashchenko and coworkers [17] have measured the relative cross section for $1s-2p$ excitation of He^+ from threshold to 300 eV and find excellent agreement with the theoretical energy dependence over the entire energy range.

Crandall [6] has suggested that theory may be over-estimating the effect of the monopole contribution in the $1s-2s$ excitation. Dolder [8] has

1s-2s excitation of He⁺ by electron impact

Fig. 1. Comparison of experimental and theoretical cross sections for excitation of He⁺ by electron impact. Circles are data of Dolder and Peart [16] and crosses are those of Dance et al. [3]. Part (a) is from a recent paper by Gien et al., J. Phys. B 17, 1123 (1984) and part (b) is from Ref. [16].

recently re-examined the experiments, and concluded that it is not impossible that the electron beam could have produced molecular ions from background gas, and that these ions could have been trapped by the space charge of the electrons, reacting with the He^+ in some mysterious way. Considering the care with which the experiment was performed, this would seem far-fetched, were it not for the fact that such an unexplained effect was observed at high electron currents in an experiment by Gregory et al. [18] on 2s-2p excitation of N^{4+} , right near 50 eV! This remains an outstanding issue, and will likely only be resolved by further experimental work.

2.2.2 Helium-Like Ions

The only He-like ion to be studied by the beams method thus far is Li^+ . Rogers and coworkers [19] made absolute measurements of the 548.5 nm radiation emitted following the spin-forbidden $1^1\text{S}-2^3\text{P}$ excitation. Near threshold the cross section is comparable in magnitude to that for 1s-2s excitation of He^+ , and shows well-defined structure due to the effect of resonances in the threshold region. The data also exhibit the expected E^{-3} dependence at high energies. The qualitative agreement with 5-state close-coupling calculations is good, but quantitative agreement with distorted-wave theory is better in this case.

2.2.3 Lithium-Like Ions

The most extensive experimental studies to date have been for the lithium isoelectronic sequence. Ions of this electronic structure have strong resonance lines, and are very prominent in the radiation emitted by

Fig. 2. Absolute cross sections for 584.5 nm emission from $1s \rightarrow n^3l$ excitation of Li^+ by electron impact, from Rogers et al. [19]. The data are compared to a number of theoretical predictions.

plasmas. Absolute cross sections have been measured for 2s-2p excitation of Be^+ , C^{3+} and N^{4+} . The Be^+ case is often cited as a benchmark for theory [20] and experiment [21]. The figure shows a comparison of the experiment with a number of theoretical calculations, the latter converging towards the measurements, as the degree of sophistication increases. A disconcerting discrepancy of about 15% still remains, however, over the entire energy range, well outside the range of absolute accuracy of the experiment (9%). In this case, the polarization of the emitted radiation was also measured, and the internal consistency check at high energies noted in section 2.1.4 could be applied. The results demonstrate the internal consistency of the experiment. This suggests that all the physics necessary to define the problem may not be included in even the most sophisticated theories. For example, it has been suggested that the role of electron-electron correlations in the target wave functions may be more important than originally thought for this seemingly simple case of a single electron outside a closed shell [22].

For 2s-2p excitation of multiply charged Li-like ions, the situation is much improved. Absolute experiments for C^{3+} [23] and N^{4+} [18] are in excellent agreement with both close-coupling and Coulomb-distorted-wave calculations over the whole energy range of the measurements. As noted by Gregory and coworkers, the increasing dominance of the Coulomb field increases the relative spacing between the $n=2$ levels and those of different n , evidently reducing the importance of correlation effects for these ions. If this trend is indeed real, it has important ramifications for the physics of high-temperature plasmas, where, at least for the present, theory must be relied upon for the more highly charged ions.

Fig. 3. Absolute experimental cross sections are compared to theoretical predictions for electron-impact excitation of the 2s-2p transition in two Li-like ions.

Fig. 4a. Measured polarization of the unresolved 313 nm multiplet emission in Be^+ as a function of electron energy, along with theoretical predictions.

Fig. 4b. Bethe plots of experimental and theoretical collision strengths versus $\log E$ for 313 nm emission from 2s-2p excitation of Be^+ . The hatched band is the experimental collision strength deduced from the polarization measurements alone, as discussed in Section 2.1.4. The bottom curve is the theoretical cascade contribution.

Some experimental information is also available for $1s-2p$ inner-shell excitation of Li-like ions via the excitation-autoionization process. In this case the excitation of an inner-shell electron is manifest in the measured total electron-impact ionization cross section as a sharp jump which onsets at the threshold for the excitation process. This mechanism was first observed experimentally by Peart and Dolder [24] in the electron-impact ionization of Ba^+ . Data now exist for six members of the lithium sequence: Be^+ [25], B^{2+} [26], C^{3+} and N^{4+} [27], O^{5+} [26-28], and Ne^{7+} [29]. The implementation of electron-cyclotron-resonance (ECR) multi-charged ion sources in crossed-beams experiments at Louvain-la-Neuve and Oak Ridge during the last year or so has made possible more accurate measurements for O^{5+} [26,28] and new data for Ne^{7+} [29]. The earlier-reported O^{5+} data from Oak Ridge [27] had large uncertainties, but suggested a larger $1s-2p$ excitation cross section than predicted theoretically. This cast doubts on the ability of theory to predict scalings of cross sections to higher ionic charges. The newer, more precise data eliminate the discrepancy at the higher charges. Table 1 is adapted from a recent paper by Crandall et al. [26], which has carefully re-analyzed the experimental data for the Li-sequence. The comparison between the various theoretical estimates for the $1s-2p$ excitation cross section just above the threshold is seen to be quite reasonable.

In estimating excitation cross sections from ionization data in this way, questions such as branching ratios for radiative decay versus autoionization, and interference between the direct and indirect channels must also be considered. These issues and other examples of excitation-autoionization will be addressed later in the discussion of electron-impact ionization.

Fig. 5. Experimental cross sections for electron-impact ionization of Li-like O^{5+} and Ne^{7+} , showing contributions due to $ls-nl$ excitation followed by autoionization, which cause an abrupt rise in the cross sections. These data are compared to a number of theoretical predictions. The solid circles for O^{5+} are new ORNL-JILA results, and the triangles and Ne^{7+} data are from the Louvain-la-Neuve group.

Table 1. $1s^2 2s \rightarrow 1s2s2l$ Excitation cross sections in 10^{-19} cm^2 .

Ion	Energy (eV)	Previously Deduced Exp.	Scaled Coulomb- Born	Jakubowicz and Moores, CBX	Six-State Close Coupling	Presently Deduced Exp.	Ratio Exp/6cc Theory
Be ⁺	125	17	23 (10.1)		9.3	20 $\pm$ 8	2.1
B ²⁺	208		6.7 (3.5)		4.1	4.0 $\pm$ 1.0	1.0
C ³⁺	325	3.2	3.7 (2.2)	3.0	2.24	2.3 $\pm$ 0.7	1.0
N ⁴⁺	460	1.8	2.0 (1.3)	2.0	1.27	1.6 $\pm$ 0.4	1.3
O ⁵⁺	612	2.8	1.1 (0.8)	1.2	0.74	0.9 $\pm$ 0.3	1.2

2.2.4 Sodium-Like Ions

The only other ionic electronic sequence where more than one member has been studied in crossed-beams experiments is that of sodium, where measurements have been made for Mg^+ [30-33] and Al^{2+} [34]. The measurements for both ions are for 3s-3p excitation of the unresolved fine-structure doublet, and have been made absolute by radiometric calibration.

The independently-absolute data for Mg^+ of the JILA and Uzhgorod groups are in agreement within their relative total uncertainties, and are also within 15% of close-coupling and distorted-wave calculations near threshold. Non-absolute measurements by Zapesoschni and coworkers [32] with an improved energy resolution of 0.3 eV show well-resolved structure in the near-threshold region due to recombination resonances. Angular differential cross sections have also been measured for this ion [33], and will be discussed in the next section.

In the case of Al^{2+} , the absolute experiment of Dunn et al. [34] and distorted-wave-with-exchange theory are in near-perfect agreement over the entire energy range of the measurements, suggesting again that theory may become more reliable for more-highly charged Na-like ions, as was the case for the Li-sequence.

2.2.5 Angular Differential Measurements

The most significant innovation in the study of ion excitation in the last few years is the development at Jet Propulsion laboratory by Chutjian [35] of an apparatus to measure inelastic angular scattering of electrons from ions. The measurements of the scattered electrons are differential

Fig. 6. Absolute cross sections near threshold for 280 nm emission from 3s-3p excitation of Mg^+ , showing structure due to recombination resonances. Graph (a) is from the Uzhgorod group [32], and graph (b) is unpublished data from the JILA group. The solid curve in (b) is a calculation by Mendoza convoluted with the experimental energy spread.

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Fig. 7. Absolute cross section for 168 nm emission from $3s-n\ell$ excitation of Na-like Al^{2+} by electron impact [34]. The solid curve is a distorted-wave-with-exchange calculation.

in both inelastic energy loss and angle. Thus far, they have studied Cd^+ [35], Zn^+ [36] and Mg^+ [33]. Their angular scattering data for 3s-3p excitation of Mg^+ at an electron energy of 35 eV is compared to the 5-state close coupling calculation of Msezane and Henry [33]. The measurements have been normalized to theory at 12° , but the agreement in shape is encouraging. Similar results for 4s-4p excitation of Zn^+ are in good agreement with close-coupling calculations. A plot of the experimental differential cross section versus electron energy at a fixed scattering angle of 14° is also given. The agreement with theory is seen to become much worse at lower electron energies, where the inelastic energy loss becomes an appreciable fraction of the incident electron energy. Whether this discrepancy indicates a problem with the theory, or the experiment, or both, is unresolved at the present time.

These differential scattering measurements from ions are technically difficult, and represent a significant achievement. Clearly, such experiments will have more to say in the next few years, and will provide new motivation to the theorists.

2.2.6 Other Ions

Some of the most reliable experimental absolute cross section data are for singly-charged, heavier ions, where the cross sections are generally larger, and the wavelengths of the transitions are in or close to the visible region of the optical spectrum, where radiometric calibration is more tractable. As pointed out by Crandall [6], 4s-4p excitation of Ca^+ by Taylor and Dunn [37] must rank as one of the most detailed experiments to be performed in atomic collision physics.

Fig. 8. Angular scattering apparatus of Chutjian and differential cross section measured as a function of scattering angle for excitation of Cd^+ at an electron energy of 35 eV. Solid curve is a close-coupling calculation by Msezane and Henry.

Fig. 9. Measured and calculated angular differential scattering cross sections for 4s-4p excitation of Zn^+ , as a function of scattering angle for fixed electron energy of 75 eV (a), and as functions of the electron energy for fixed scattering angles (b). The experimental data in (b) correspond to an angle of 14°.

Excitation experiments for positive atomic ions from intersecting-beams experiments up to 1982 were tabulated by Dolder [8]. Apart from the work already mentioned, this author is aware of only two other ions for which measurements have been made since that review.

The JILA group of Stefani and coworkers [38] measured absolute cross sections for emission of 141.4 nm radiation resulting from $4^1S - 4^1P$ excitation of Ga^+ . Their data were about 60% below the Gaunt-factor prediction near threshold, and 20% above it at high energies. No other theoretical predictions were available.

Hane and coworkers at Nagoya University have recently developed a crossed beams apparatus to study electron-impact excitation of ions, and have reported absolute cross sections for excitation of eight different transitions in Cd^+ which are relevant to the the formation of the 441.6 nm laser line [39,40]. Again, no theory was available, and no comparisons were made to the Gaunt factor formula.

2.3 Excitation Rate Coefficients from Plasmas

Collisional excitation rate coefficients have been determined experimentally for a number of ions by detecting absolutely the spectral emission from well-behaved and well-diagnosed plasmas. The reviews of Kunze [4] and Gabriel and Jordan [41] are standard references for such experiments. Work on Li-like ions by Kunze and Johnson [42] and by Boland and coworkers [43] are representative examples of some of the careful work which has been done. Results for 2s-2p excitation of C^{3+} and N^{4+} are consistent with those obtained from crossed-beams measurements.

The collisional excitation rate coefficient $\alpha(T)$ is defined as follows:

Fig. 10. Absolute cross sections for 141.4 nm emission resulting from $4^1S - 4^1P$ excitation of Ga^+ , from [38]. Solid curve is the Gaunt-Factor or g-formula.

Fig. 11. Absolute cross sections for $5^2\text{S}-5^2\text{P}^0$ excitation of Cd^+ , compared to the $\bar{g}$ -formula prediction. The solid points are the absolute data of Hane et al. [40] for the $2\text{P}^0_{3/2}$ level. The square is the integrated differential cross section measured by Chutjian [35] for the unresolved $2\text{P}^0_{3/2}, 2\text{P}^0_{1/2}$ doublet. The triangle is the estimate of the latter for the $2\text{P}^0_{3/2}$ state alone, assuming cross section ratios proportional to statistical weights.

Fig. 12. Rate coefficients for excitation of N^{4+} by electron impact, obtained by the plasma spectroscopy technique [43]. Solid and dashed curves represent close-coupling calculations, and the g-formula, respectively. Rate coefficients calculated from the crossed-beams measurements shown in Fig. 3 are coincident with the solid curve.

$$\alpha(T) = \int_{E_0}^{\infty} v \sigma(E) f(E) dE \quad 2.10$$

where v is the electron velocity, E the electron energy, E_0 is the threshold energy for the process, and $f(E)$ is the electron energy distribution function, which is usually a Maxwellian with some electron temperature, T . The rate coefficient is expressed in units of cm^3s^{-1} .

Magnetically confined plasmas such as pinches have been the most widely used for excitation rate determinations. The method is based on a number of assumptions about the behavior of the plasma, the most important of which form part of the basis for the so-called coronal-equilibrium model. These are that the state which is being excited to produce the relevant radiation is populated only by excitation from the initial level in collisions with electrons, and that the excited level is depopulated only by radiative decay. No other processes should play a role in the dynamics of the states involved. The extent to which these conditions apply must be considered in each case, and an allowance made for any departures.

To determine the rate coefficient, the densities of the electrons and ions in the initial state must be determined, and also the electron temperature. All of these must be homogeneous over the radiating volume. In addition, the photon detection system must be absolutely calibrated, as in the intersecting beams method. Thus excitation rate coefficients determined in this way are subject to large uncertainties, and the averaging over a Maxwellian energy distribution causes any structure in the cross section, and the physical information contained therein, to be lost. Nevertheless, the method is important in that it has provided the only available information on ions in high ionization stages, and improvements have been made in plasma diagnostic techniques to characterize the plasma.

Experimental rate coefficients have been reported recently for Li-like Ne^{7+} by the Ruhr University group of Chang et al. [44]. Their rate coefficients at 75 eV for 2s-3l and 2s-4l excitation agree with close-coupling and Coulomb-Born calculations within the experimental uncertainty of 50%.

The Maryland group of Wang et al report excitation rate measurements for a number of strong transitions in Fe^{9+} [45], and in Fe^{7+} , Fe^{8+} and Fe^{10+} [46] from a theta-pinch plasma of hydrogen seeded with 1% Fe. The absolute uncertainties of their rate coefficients are estimated to be 30-40%, and their rates generally agree with distorted-wave theory within these limits.

2.4 Other Methods

It is clear that because of low photon intensities and the difficulties of calibration in the extreme ultraviolet and soft X-ray regions, new experimental approaches are needed to benchmark theory for higher ionization stages. Such a course is being pursued by the JILA group led by G. H. Dunn. They are constructing a merged electron-ion beams apparatus in which the excitation process will be detected by electron energy-loss spectroscopy. The method is limited to the near-threshold region, but that is where the cross section is usually largest, the most important in plasmas, and where theory is least reliable. Collection of the scattered electrons will be facilitated by immersion of the interaction region in an axial magnetic field. The inherent advantage of the merging-beams technique of improved energy resolution promises important experimental information about the effects of resonances, which thus far have been barely discernable in crossed-beams experiments.

Fig. 13. Plasma rate coefficient measurements for Li-like Ne^{7+} as a function of electron temperature, from [44]. Solid curves are 5-state close-coupling calculations, and dashed curves are Coulomb-Born results.

3. ELECTRON-IMPACT IONIZATION

3.1 Fundamentals

3.1.1 Ionization Mechanisms

Ionization is a complex process, since a large number of mechanisms can cause the ejection of electrons from bound states of atomic systems. The most important ionization mechanisms which have been identified for ions are summarized below, and examples of each are given.

a. Direct Ionization:

In direct or "knock-on" ionization, the collisional transfer of energy to the target electron exceeds the binding energy, causing ejection. The probability for ejection of more than a single electron by this mechanism ($n > 1$) is relatively small. In the case of He^+ , only direct ionization is possible, and the results of the first crossed-beams experiment to measure electron-impact ionization of an ion of Dolder and Peart [2] serves as a good example of the behavior of the direct ionization cross section.

b. Ionization-Autoionization:

The ejection of a more tightly bound inner-shell electron leaves an ion in a core-excited state which can subsequently autoionize, resulting in the ejection of one or more additional electrons, depending on the excitation energy of the "hole" state, and the branching ratio for radiative versus

Fig. 14. Cross section for electron-impact ionization of He^+ as a function of electron energy in threshold units. Points are crossed-beams measurements of Dolder et al. [2], and curve is distorted-wave exchange calculation of Younger.

Fig. 15. Experimental cross sections for double ionization of Ar^{2+} (open circles), Ar^{3+} (triangles) and Ar^{4+} (solid circles), showing dominance of 2p-ionization-autoionization. The data are from the Giessen and ORNL groups.

Auger decay (fluorescence yield). In this example, the excited state $(X^{+q+1})^*$ decays by single Auger emission, yielding net double ionization. For deeper inner-shell vacancies, successive Auger emissions, or simultaneous multiple Auger emissions may also be possible, resulting in net multiple ionization. The ionization-autoionization process is the dominant mechanism for multiple ionization of ions. A comparison of experimental cross sections for electron-impact double ionization of Ar^{2+} , Ar^{3+} and Ar^{4+} from a recent paper by Pindzola et al. [47] shows the dominance of 2p ionization-autoionization for these ions.

c. Excitation-Autoionization:

The electron-impact excitation of an ionic inner-shell electron can also produce a core-excited ion which can decay by the Auger process, leading to net ionization. As noted in Section 2.2.1 the cross section for excitation of an ion by electron impact is finite and most often largest at threshold. Thus the excitation-autoionization process for a strong, well-isolated transition often produces a distinctive jump in the measured total ionization cross section at the threshold energy for the excitation process. As noted earlier in Section 2.2.3, this mechanism can provide valuable information about the excitation process. The first experimental demonstration of this process by Peart and Dolder [24,48] for singly charged alkaline earth ions remains one of the more dramatic examples of its potentially dominant role in ionization.

Fig. 16. Role of inner-shell excitation-autoionization in electron-impact ionization of the alkaline-earth ions. The curves are experimental data of Peart and Dolder [24,48], except for Be^+ , which is from Falk and Dunn [Phys. Rev. A 27, 754 (1983)]. The sharp changes in slope indicate the onset of the excitation-autoionization process.

d. Resonant-Recombination Double Autoionization:

3.4

In this case the incident electron resonantly recombines with the target ion to form a doubly-excited intermediate state, which subsequently decays by two-step Auger emission. The excitation process here is analogous to dielectronic recombination, except that it is associated with the excitation of an inner-shell electron. This ionization mechanism was first postulated by LaGattuta and Hahn [49] in 1981, and is predicted to make a non-negligible contribution to the electron-impact ionization of Fe^{15+} . A large contribution due to the excitation-autoionization process is also predicted for this Na-like system. Henry and Msezane [50] have suggested a variation on this resonant process whereby the doubly-excited intermediate state decays by simultaneous double Auger emission, which they have labelled "auto-double ionization".

3.1.2 Threshold Behavior

The threshold ionization of atoms by electron impact has received considerable attention, both experimentally and theoretically, and is often considered a subfield in itself. According to the Wannier theory [51,52], the threshold behavior is primarily determined by the Coulomb interaction of the two outgoing electrons, a classical treatment of which leads to a threshold cross section:

$$\sigma_{\text{ion}} \propto (E-I)^n, \quad n = \frac{1}{4} \left[\left(\frac{100Q-9}{4Q-1} \right)^{1/2} - 1 \right] \quad 3.5$$

Fig. 17. Theoretical cross sections for electron-impact ionization of Fe^{15+} , from Ref. 49. Solid curve is the Lotz formula for direct ionization, with the dashed curve added to represent excitation-autoionization contributions. The hatched area is added to represent the resonant-recombination double-autoionization contribution.

where E is the incident electron energy, I is the ionization potential and Q is the charge on the residual ion. For neutral atoms, $Q=1$ and $n=1.127$, a value which has been verified experimentally for He to a high level of precision [53]. For single ionization of ions of initial charge q , the prediction for n is given in the table below.

<u>q</u>	<u>n</u>
1	1.056
2	1.036
3	1.026
10	1.009
100	1.001

The predicted departures from a linear ionization onset with energy for ions are very small, and decrease with increasing ionic charge. While nearly all existing experiments for ions are consistent with these predictions, none is of sufficient precision to quantify such small departures from linearity.

3.1.3 High-Energy Behavior

At asymptotically high energies, as was the case for dipole-allowed excitation, the energy dependence of the ionization cross section is given by the well-known Bethe form:

$$\sigma = \frac{A}{E} \ln (BE) \quad (A, B \text{ are constants}) \quad 3.6$$

This dependence is expected even when indirect ionization mechanisms such as excitation-autoionization make appreciable contributions to the ionization cross section, since these must fall off as $\ln(E)/E$ or faster, depending on the type of excitation (see Section 2.1.2).

Fig. 18. Experimental cross sections for electron-impact ionization of He^+ (1s) show the expected near-linear onset from the 54.4 eV threshold. Figure is taken from DeFrance et al. [J. Phys. B 14, 103 (1981)]. Solid points are their results, crosses are the data of Dolder et al. [2] and open circles are data of Peart et al. [J. Phys. B 2, 1347 (1969)].

3.1.4 Predictor Formulae

A number of formulae have been proposed to predict cross sections for electron-impact ionization of ions, beginning with the classical theory of J. J. Thomson [54] in 1912. As noted by Salzborn [7], this theory has serious inadequacies, but provided useful information about approximate scalings of cross sections.

a. The Lotz Formula

The most successful and extensively used predictor formula for modelling of plasmas is that of Lotz [55]:

$$\sigma(E) = \sum_{j=1}^3 a_j r_j \frac{\ln(E/I_j)}{E I_j} \{1 - b_j \exp[-c_j(E/I_j - 1)]\} \quad 3.7$$

where

E = incident electron energy in eV

I_j = ionization energy of subshell j in eV

r_j = number of electrons in subshell j

$\sigma(E)$ = ionization cross section in cm^2

a_j , b_j , and c_j are constants determined by experiment, theory, or educated guesswork. Values for these are tabulated for a number of ions in W. Lotz, Z. Phys. 216, 241-247 (1968); Z. Physik 220, 466-472 (1969) [56]. For ions of charge 4 or greater, it is customary to set $b_j = c_j = 0$ and $a_j = 4.5 \times 10^{-14}$, which gives the usual one-parameter Lotz formula.

The Lotz semiempirical formula is based in part on Coulomb-Born calculations for hydrogenic ions, and has the correct Bethe energy dependence at high energies. It also approximates very closely the expected linear onset in the near-threshold region, as discussed in the previous section. As will be seen in examples later, the Lotz prediction is generally reliable to within 25% or so in predicting the direct ionization cross section.

The Lotz formula includes only direct ionization processes. As we have seen, indirect ionization mechanisms such as excitation-autoionization can make important contributions to the total ionization cross section, and even dominate in some cases.

b. The Burgess-Chidichimo Formula

Burgess and Chidichimo [57] have recently proposed a general empirical formula similar to that of Lotz which allows for inner-shell excitation-autoionization. Their formula is

$$\sigma(E) = c \sum_j a_j (I_H/I_j)^2 (I_j/E) \ln(E/I_j) W(E/I_j) \pi a_0^2 \quad 3.8$$

where

$$I_H = 13.6058 \text{ eV}$$

$$a_0 = 5.2917 \times 10^{-9} \text{ cm}$$

$$W(E/I_j) = \begin{cases} 0 & E < I_j \\ \ln(E/I_j) & E > I_j \end{cases} \quad n \ I_j/E$$

n is given by Eq. 3.5 ($n \approx 1$)

$C = 2.30$ is an empirical constant

I_j = ionization (or excitation) energy of the j^{th} shell (or subshell)

a_j = occupation number of j^{th} shell (or subshell)

The function $W(E/I_j)$ assures the Wannier threshold behavior discussed in the previous section, but approaches unity at very high energies, thus preserving the asymptotic Bethe energy dependence. They determined the constant C empirically by comparison to all the available experimental cross section data. A value of $C=2.30$ was observed to fit the data with a 23% rms deviation.

Excitation-autoionization is included in the same manner as direct inner-shell ionization, except that the lowest excitation threshold energy for the subshell is used for E_i . Thus the finite cross section for ion excitation at threshold cannot be accounted for. Nevertheless, their approach does make some allowance for excitation-autoionization, and in cases where there are a number of excitations from a subshell occurring over a range of threshold energies, it can give reasonable predictions for the cross section. As is the case for inner-shell ionization, the lowest excitation threshold energy must be known.

The Burgess-Chidichimo formula must be considered an improvement over the Lotz formula, since the empirical constant is chosen from a much broader data base, and since the contributions of direct and indirect ionization have been separated. A comparison of their empirical prediction with scaled-Coulomb-Born calculations is given for Na-like Fe^{15+} , where $3s\text{-}n\ell$ excitation-autoionization is expected to make a substantial contribution.

3.1.5 Theoretical Approaches

Since ionization theory will be addressed specifically by the lectures of Pindzola, only a list of the methods which have been applied to

ionization of ions will be given here. The introduction to theoretical approaches given by Salzborn [7] is especially recommended to the experimentalist or non-specialist. In roughly increasing order of sophistication, some of the theoretical methods which have been applied to electron-impact ionization are:

Classical Binary Encounter

Impact Parameter Method

Plane-Wave Born Approximation

Exchange-Classical Impact-Parameter Method

Coulomb-Born Approximation

Coulomb-Distorted-Wave Approximation

Close-Coupling/Coulomb-Born approximation.

As in excitation, inclusion of effects such as exchange and electron-electron correlation within a given calculation can change the ordering. Contributions due to excitation-autoionization have generally been estimated by calculating separately the inner-shell excitation cross section, scaling it by the appropriate branching ratio for autoionization versus radiative decay, and simply adding this to the ionization cross section. The Close-Coupling/Coulomb-Born method [58] is an attempt to include, in a unified treatment, both direct and indirect ionization. Thus, implicitly accounted for are possible effects due to interference between direct and indirect ionization channels, as well as resonances.

3.2 Experimental Methods

Again, experimental techniques for electron-impact ionization of ions will be addressed specifically by P. Defrance, and only a few comments are

in order here, in order to place the results to be presented into a proper perspective. A recent review by Dunn [60] gives an insightful and critical discussion of these methods, and of the history and current status of experimental research in this field.

3.2.1 Intersecting-Beams Method

As was noted in the case of excitation, the most accurate and detailed data on the ionization process has come from the intersecting-beams method. In the case of ionization, all of the product ions may in principle be collected and detected with unit efficiency, giving an advantage in signal of three orders of magnitude or more over excitation experiments. Thus both the sensitivity and accuracy of the method is improved. Differences of more than 10% between cross section measured by different groups are uncommon. The beams method also offers the highest energy resolution, and thus far has provided the only information about the onset of indirect mechanisms, or the role of metastable states.

3.2.2 Plasma Spectroscopy Method

In this technique, ionization rate coefficients (see Eq. 2.10) are determined from measurements of the time evolution of the intensity of spectral-line emission from a well-diagnosed plasma. The same requirements and constraints apply that were discussed for excitation rates in Section 2.3, with the exception that absolute calibration of the photon detectors is not required to deduce ionization rates. These rate coefficients are adjustable parameters in a set of coupled rate equations describing the time histories of properly chosen spectral lines representing each of the ionization stages of the ion of interest. Although such measurements are

generally considered to be less accurate than the beams data, and give little or no information about specific ionization mechanisms, the only published data on the higher ionization stages ($q > 7$) have been obtained using either this or the related trapped ion method.

3.2.3 Trapped-Ion Method

Absolute cross sections for electron-impact ionization have also been obtained by trapping ions in some combination of electric and/or magnetic fields, and bombarding them with energetic electrons. The most definitive application of this concept is the work of Donsals and Ovsyannikov [59], who analyzed the time histories of the charge states of trapped ions produced in an electron-beam ion source (EBIS). The charge-state distribution is determined by extracting the ions and performing a time-of-flight analysis. The modeling and fitting procedure for deducing the rate coefficients is similar to the plasma spectroscopy method outlined above, but the method offers the advantage of a monoenergetic, well-defined electron beam, and thus yields cross sections rather than Maxwellian-averaged rate coefficients. The accuracy of the data obtained are intermediate between the intersecting-beams and plasma-spectroscopic methods. For the heavier ions, multiple ionization has been shown by the beams experiments to be non-negligible, and thus the sequential single-ionization model which has been applied may be inadequate for determining accurate cross sections.

3.3 Experimental Results for Ionization

Unlike the situation for electron-impact excitation, there has been vigorous experimental activity and substantial progress made in electron-impact ionization during the last several years. It will be impossible to

give a comprehensive review of this work during the time allotted, so specific examples will be presented which are particularly representative of various aspects of the ionization process. Emphasis will be given to work reported since the last meeting of this series.

3.3.1 Single Ionization

The hydrogen-like ion is the simplest for which electron-impact ionization can occur, and such collisions may be regarded as a true three-body systems. Since only direct ionization is possible, measurements for H-like ions provide an important bench mark for theory. The Z^{-4} scaling of the cross section as a function of electron energy in threshold units, predicted by the Coulomb-Born and distorted-wave approximations, is compared to the available data. The experimental results for He^+ are crossed-beams data of Dolder et al. [2], and the data for the higher- q ions are from the trapped-ion measurements of Donets and Osvyannikov [59].

The role of $ls-nl$ excitation-autoionization (EA) in electron-impact ionization of Li-like ions was discussed in Section 2.2.3, with regard to the information it can provide about the excitation process. We consider here its relative importance as an ionization mechanism. The crossed-beams data of Falk and Dunn [25] for Be^+ show the relatively small contribution in this case. They find a good fit to the data by adding the g -formula for the excitation cross section to the Lotz-formula scaled by 0.95. Scaled-Coulomb-Born calculations do not compare favorably with the measurements in this case, even at high energies, where they underestimate them by about 30%.

Fig. 19. Comparison of scaled electron-impact ionization cross sections plotted in threshold energy units with distorted-wave-exchange calculations for $Z=128$. $\times$ - He^+ [2]; $\circ$ - C^{5+} , $\square$ - N^{6+} , $\triangle$ - O^{7+} , $\blacktriangle$ - Ne^{9+} , $*$ - Ar^{17+} [59]. Figure is taken from [60].

Fig. 20. Experimental cross sections for electron-impact ionization of Li-like Be^+ , compared to the sum of the Lotz and g formulae for direct ionization and $1s-nl$ excitation-autoionization, respectively.

Fig. 21. Comparison for the Li-isoelectronic sequence of experimental data and theoretical predictions for the ratios of the maximum $1s-nl$ EA contribution to the peak direct ionization cross section.

Since accurate experimental data now exist for six members of the Li sequence, it is instructive to reconsider the relative importance of the $1s-nl$ excitation-autoionization mechanism for these ions. The graph shows the ratio of the EA contribution just above its threshold to the peak direct ionization cross section, as a function of nuclear charge Z . The points are experimental [25,26,29], and the solid curve results from taking the ratio of close-coupling excitation cross sections to the measured peak direct ionization cross section. The predicted trend seems to be observed by the measurements, although the latter are systematically higher.

For higher Z , it is no longer appropriate to ignore the radiative decay of the $1s2s2l$ core-excited states. This occurs because the radiative decay rates scale roughly as Z^4 , while the autoionizing rates are almost independent of Z . The branching ratio for autoionization versus radiative decay must always be considered when estimating contributions of inner-shell excitations to ionization.

Systematic studies along ionic sequences can be particularly useful in identifying trends, and assessing the importance of indirect ionization mechanisms. Griffin and coworkers [61] have completed a combined experimental-theoretical study of single ionization in the Xe-isonuclear sequence, from Xe^{2+} to Xe^{6+} . A comparison of their experimental cross sections with Lotz predictions for direct ionization show large contributions due to indirect ionization, which increase in relative importance with increasing ionic charge. Distorted-wave calculations were made for excitations of the type $4d-nl$ (where $nl=4f$, $5d$ and $5f$), which were found to account for most of the indirect contributions. The Xe^{6+} ion has the

Fig. 22. Comparison of experimental cross sections for electron-impact ionization of Xe^{q+} ions ($q=2-6$), showing increasing dominance of excitation-autoionization with increasing ionic charge.

Fig. 23. Calculated energy levels important in 4d excitation-autoionization of Xe^+ , Xe^{3+} and Xe^{5+} . The hatched region indicates the ionization continuum.

Fig. 24. Comparison to experiment of distorted-wave 4d-nl excitation cross sections added to the Lotz direct ionization cross section (long-dashed curve) for Xe^{6+} . The curve marked NA represents the sum of the 4d excitations which are non-autoionizing. The short-dashed curve is a convolution of the theory with the experimental electron energy distribution.

simplest electronic structure ($4d^{10} 5s^2$), and the agreement with experiment is seen to be excellent in this case.

All these Xe-isonuclear data show earlier onsets of the EA process than is predicted by theory, and are suggestive of the role of the resonant-recombination double-autoionization process. Griffin et al. made calculations of this process for the Xe^{6+} case, but found that although the recombination cross section was appreciable, the branching to double autoionization was too small (0.05) to account for the observed features in the ionization cross section in this case.

3.3.2 Multiple Ionization

Cross sections for the ejection of more than a single electron from an ion in an electron-ion collision were first reported in 1980 by Muller and Frodl [62] for Ar^{q+} ($q=1,2,3$). They concluded that ejection of a single L-shell electron, followed by autoionization, was responsible for most of the observed multiple ionization. Figure 15 shows some of this data. For complex ions, this ionization-autoionization mechanism becomes relatively more important for the higher ionization stages, since the cross sections for inner-shell ionization depend only weakly on charge state, while those for the ejection of outer-shell electrons fall off roughly as I_p^{-2} . The direct ejection of more than one outer-shell electron in a single collision is not a first-order process, and quantum-mechanical methods have not yet been developed to treat this problem. The only method which has been suggested is the classical binary-encounter approximation [63].

The Giessen group have recently remeasured the cross sections for double ionization of Ar^+ and Ar^{4+} with higher precision [64]. For Ar^{4+}

Fig. 25. Experimental cross sections for electron-impact double ionization of Ar^{4+} , from Ref. 64. Solid and open circles are data from the Giessen and Oak Ridge groups, respectively. Solid curve is the sum of binary-encounter direct-double ionization (dashed) and Lotz 2s and 2p direct ionization cross sections. Chain-dashed curve is the binary-encounter estimate for 2l direct ionization.

they measure a small double-ionization cross section at energies below the 320 eV threshold for 2p ionization. To account for this, they apply the binary-encounter model for ejection of two outer-shell electrons. This small cross section added to the 2s and 2p direct ionization cross sections predicted by the Lotz formula gives a reasonable account of the experimental data, although the classical model overestimates the low-energy contribution.

Pindzola and coworkers [47] have recently published a combined experimental-theoretical study of double ionization of quadruply-charged noble gas ions, and also have examined the double-ionization data from the Giessen group for Xe^{9+} ions. On the basis of distorted-wave calculations, they conclude that double ionization of rare-gas ions is dominated by the inner-shell ionization-autoionization mechanism.

Their calculations and the Lotz formula for the sum of 3d and 3p ionization are compared to the experimental data for Kr^{4+} in the figure. A blowup of the threshold region shows an almost negligible contribution from direct double ionization, which has a threshold of 141 eV. The distorted wave theory is in reasonable agreement with experiment up to about 300 eV, but overestimates the peak by about 30%.

A similar comparison with experimental data from the Oak Ridge and Giessen groups for double ionization of Xe^{4+} shows the dominant contribution of 4d and 4p ionization-autoionization in this case. In the configuration-averaged calculation, the fraction of 4d levels which autoionize is difficult to assess. The upper curve represents the sum of cross sections for ionization of all 4p and 4d levels, while the lower results from multiplication of the total by the fraction of 4d levels which

Fig. 26. Relevant energy levels for ionization-autoionization of Kr⁴⁺ and Xe⁶⁺. Comparison of experiment and theory for double ionization of Kr⁴⁺ and Xe⁴⁺. Solid points are Oak Ridge data and open points are data from the Giessen group (all from Ref. 47).

Fig. 27. Comparison of experimental cross sections for electron-impact double ionization of Xe^+ and I^+ . Curves in (a) represent a fit of the Lotz-formula to the low and high-energy data. Data in (b) represent the residual "hump" obtained by subtracting the solid curves in (a) from the total. Solid curve in (b) is the measured 4d-photoionization cross section [66], and dashed curve is the 4d Lotz cross section (all from Ref. 65).

autoionize (1/3). This assumes that the ionization cross sections scale with statistical weights, which may not be the case. Complicated level-by-level calculations would be required to resolve this issue. In any case, the experimental data fall between these two extremes, and it may be safely assumed that 4d and 4p ionization-autoionization dominate the double ionization cross section in this case also. Their distorted-wave calculations for the Xe^{9+} ions are strongly influenced by term-dependence in the ejected-electron continuum, and by ground-state correlations.

Another interesting manifestation of the clear signature of the ionization-autoionization process in multiple ionization was reported by Achenbach and coworkers [65], who observed pronounced resonance-like "humps" in the experimental double ionization cross sections for Xe^+ and I^+ . They demonstrated the striking correspondence between these structures and measured 4d photoionization cross sections for Xe atoms [66]. Why this correspondence should exist is not yet fully understood, but it is likely that the answers lie in the detailed atomic structures of these complex ions.

3.4 General Remarks about Electron-Impact Ionization of Ions

Analysis of the increasing body of experimental data on the ionization of positive atomic ions by electron impact leads one to some general conclusions about the behavior of the cross sections, and the relative importance of the various ionization mechanisms. A few such observations are listed below.

1. Direct single ionization is quite well represented by theory, and predicted by semiempirical formulae with reasonable accuracy.

2. Direct multiple ionization is usually negligible in most cases.
3. Inner-shell excitation-autoionization can be an important or even dominant ionization mechanism in some cases, and negligible in others.
4. It is probable that resonant-recombination multiple-autoionization or related resonant processes are non-negligible for complex ions whenever the excitation-autoionization process is dominant.
5. Inner-shell ionization-autoionization is the dominant multiple ionization mechanism for all ions.
6. Indirect ionization mechanisms become relatively more important as the ionic charge increases along an isoelectronic or isonuclear sequence.
7. Contributions to ionization from indirect mechanisms are generally more significant for ions with complex electronic structure than for simple ions.
8. Multiple ionization of partially-stripped heavy ions is not always negligible compared to single ionization, and should be considered in accurate plasma models, or determination of excitation and ionization rate coefficients.

REFERENCES

1. M.F.A. Harrison, "The Plasma Boundary region and the Role of Atomic and Molecular Processes," in Atomic and Molecular Physics of Controlled Thermonuclear Fusion, ed. C. J. Joachain and D. E. Post, NATO Advanced Study Institute Series B: Physics, Vol. 101 (Plenum, New York and London, 1983), pp. 473-475.
2. K. Dolder, M.F.A. Harrison and P. C. Thoneman, Proc. Roy. Soc. A 264, 367 (1961).
3. D. F. Dance, M.F.A. Harrison and A.C.H. Smith, Proc. Roy. Soc. A 290, 73 (1966).
4. H-J. Kunze, Space Sci. Rev. 13, 565 (1972).
5. F. A. Baker and J. B. Hasted, Phil. Trans. Roy. Soc. A 261, 33 (1966).
6. D. H. Crandall, "Electron-Impact Excitation of Ions," in Physics of Ion-Ion and Electron-Ion Collisions, ed. F. Brouillard and J. W. McGowan, NATO Advanced Study Institute Series B: Physics, Vol. 83 (Plenum, New York and London, 1983), pp. 201-238.
7. E. Salzbom, "Electron-Impact Ionization of Ions," ibid., pp. 239-277.
8. K. T. Dolder, "Experimental Aspects of Electron-Impact Ionization and Excitation of Positive Ions," in Atomic and Molecular Physics of Controlled Thermonuclear Fusion, ed. C. J. Joachain and D. E. Post, NATO Advanced Study Institute Series B: Physics, Vol. 101 (Plenum, New York and London, 1983), pp. 213-243.

9. D. H. Crandall, "Electron-Ion Collisions," in Atomic Physics of Highly Ionized Atoms, ed. R. Marrus, NATO Advanced Study Institute Series B: Physics, Vol. xxx (Plenum, New York and London, 1983), pp. 399-453.
10. D.W.O. Heddle, J. Phys. B 12, 489 (1979).
11. M. J. Seaton, "The Theory of Excitation and Ionization by Electron Impact," in Atomic and Molecular Processes, ed. D. R. Bates (Academic, New York, 1962), p. 374.
12. H. Van Regemorter, Astrophys. J. 136, 906 (1962).
13. S. M. Younger and W. L. Wiese, J. Quant. Spectrosc. Rad. Transfer 22, 161 (1979).
14. R.J.W. Henry, "Excitation of Positive Ions by Electron Impact," Phys. Reports 68, 1 (1981).
15. W. D. Robb, "Theoretical Studies of Electron Impact Excitation of Positive Ions," in Atomic and Molecular Processes in Controlled Thermonuclear Fusion, ed. M.R.C. McDowell and A. M. Ferendeci, NATO Advanced Study Institute Series B: Physics, Vol. B53 (Plenum, New York and London, 1980), pp. 245-265.
16. K. T. Dolder and B. Peart, J. Phys. B 6, 2415 (1973).
17. A. I. Dashchenko, I. P. Zapesochnyi, A. I. Imre, V. S. Bukstich, F. F. Danch and V. A. Kel'man, Sov. Phys. JETP 40, 249 (1975).

18. D. C. Gregory, G. H. Dunn, R. A. Phaneuf and D. H. Crandall, Phys. Rev. A 20, 410 (1979).
19. W. T. Rogers, J. Olsen and G. H. Dunn, Phys. Rev. A 18, 1353 (1978).
20. M. A. Hayes, D. W. Norcross, J. B. Mann and W. D. Robb, J. Phys. B 10, L429 (1977).
21. P. O. Taylor, R. A. Phaneuf and G. H. Dunn, Phys. Rev. A 22, 435 (1980).
22. D. W. Norcross, private communication (1984).
23. P. O. Taylor, D. C. Gregory, G. H. Dunn, R. A. Phaneuf and D. H. Crandall, Phys. Rev. Lett. 39, 1256 (1977).
24. B. Peart and K. Dolder, J. Phys. B 1, 872 (1968).
25. R. A. Falk and G. H. Dunn, Phys. Rev. A 27, 754 (1983).
26. D. H. Crandall, R. A. Phaneuf, D. C. Gregory, A. M. Howald, D. W. Mueller, T. J. Morgan, G. H. Dunn and R. J. W. Henry, "Electron-Impact Excitation of B^{2+} and O^{5+} : Excitation-Autoionization of Li-like Ions," submitted to Phys. Rev. A (1985).
27. D. H. Crandall, R. A. Phaneuf, B. E. Hasselquist and D. C. Gregory, J. Phys. B 12, L249 (1979).
28. P. Defrance, S. Chantrenne, S. Rachafi, D. Belic, D. Gregory and F. Brouillard, Proc. 2nd Eur. Conf. Atom. Mol. Phys. (ECAMP), Amsterdam (1985).

29. S. Chantrenne, P. Defrance, S. Rachafi, D. Belic and F. Brouillard, XIV ICPEAC, Abstracts of Contributed Papers, Palo Alto, CA (1985), p. 299.
30. I. P. Zapesochnyi, V. A. Kel'man, A. I. Imre, A. I. Dashchenko and F. F. Danch, Sov. Phys. JETP 42, 989 (1976).
31. D. S. Belic, G. H. Dunn, T. J. Morgan, D. W. Mueller and C. Timmer, Phys. Rev. Lett. 50, 339 (1983).
32. I. P. Zapesochnyi, A. I. Dashchenko, V. I. Frontov, A. I. Imre, A. N. Gomonal, V. I. Len'del, V. T. Navrotskii and E. P. Sabad, JETP Lett. 39, 51 (1984).
33. I. D. Williams, A. Chutjian, A. Z. Msezane and R. J. W. Henry, XIV ICPEAC, Abstracts of Contributed Papers, Palo Alto, CA (1985), p. 289.
34. D. S. Belic, R. A. Falk, G. H. Dunn, D. Gregory and C. Cisneros, Bull. Am. Phys. Soc. 26, 1315 (1981), unpublished data.
35. A. Chutjian, Phys. Rev. A 29, 64 (1984).
36. A. Chutjian, A. Z. Msezane and R. J. W. Henry, Phys. Rev. Lett. 50, 1357 (1983).
37. P. O. Taylor and G. H. Dunn, Phys. Rev. A 8, 2304 (1973).
38. G. Stefani, R. Camilloni, G. H. Dunn and W. T. Rogers, Phys. Rev. A 25, 2966 (1982).
39. K. Hane, T. Goto and S. Hattori, Phys. Rev. A 27, 124 (1983).

40. K. Hane, T. Goto and S. Hattori, J. Phys. B 16, 629 (1983).
41. A. H. Gabriel and C. Jordan, "Interpretation of Spectral Intensities from Laboratory and Astrophysical Plasmas," in Case Studies in Atomic Collision Physics II, ed. E. W. McDaniel and M. R. C. McDowell, North Holland, Amsterdam (1972), pp 209-291.
42. H.-J. Kunze and W. D. Johnson III, Phys. Rev. A 3, 1384 (1981).
43. B. C. Boland, F. C. Jahoda, T. J. L. Jones and R. W. P. McWhirter, J. Phys. B 3, 1134 (1970).
44. C. C. Chang, P. Greve, K.-H. Kolk and H.-J. Kunze, Physica Scripta 29, 132 (1984).
45. J. S. Wang, R. U. Datla and H. R. Griem, Phys. Rev. A 29, 1558 (1984).
46. J. S. Wang and H. R. Griem, Phys. Rev. A 27, 2249 (1983).
47. M. S. Pindzola, D. C. Griffin, C. Bottcher, D. H. Crandall and D. C. Gregory, Phys. Rev. A 29, 1749 (1984).
48. B. Peart and K. T. Dolder, J. Phys. B 8, 56 (1975).
49. K. J. LaGattuta and Y. Hahn, Phys. Rev. A 24, 2273 (1981).
50. R.J.W. Henry and A. Z. Msezane, Phys. Rev. A 26, 2545 (1982).
51. G. Wannier, Phys. Rev. 90, 817 (1953).
52. F. H. Read, J. Phys. B 17, 3965 (1984).

53. S. Cvejanovic and F. H. Read, J. Phys. B 7, 1841 (1974).
54. J. J. Thomson, Phil. Mag. 23, 449 (1912).
55. W. Lotz, Z. Physik 206, 205 (1968).
56. W. Lotz, Z. Physik 216, 241 (1968); *ibid* 220, 466 (1969).
57. A. Burgess and M. C. Chidichimo, Mon. Not. Roy. Astr. Soc. 203, 1269 (1983).
58. B. Jakubowicz and D. L. Moores, J. Phys. B 14, 3733 (1981).
59. E. D. Donets and V. P. Ovsyannikov, Sov. Phys. JETP 53, 466 (1981).
60. G. H. Dunn, "Electron-ion Ionization" in
61. D. C. Griffin, C. Bottcher, M. S. Pindzola, S. M. Younger, D. C. Gregory, and D. H. Crandall, Phys. Rev. A 29, 1729 (1984).
62. A. Müller and R. Frodl, Phys. Rev. Lett. 44, 29 (1980).
63. M. Gryzlinski, Phys. Rev. 138, A336 (1965).
64. A. Müller, K. Tinschert, C. Achenbach, and E. Salzborn, J. Phys. B 18, 3011 (1985).
65. C. Achenbach, A. Müller, E. Salzborn, and R. Becker, Phys. Rev. Lett. 50, 2070 (1983).
66. R. Haensel, G. Keitel, P. Schreiber, and C. Kunz, Phys. Rev. 188, 1375 (1969).