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THE PHYSICS OF IONIZED GASES

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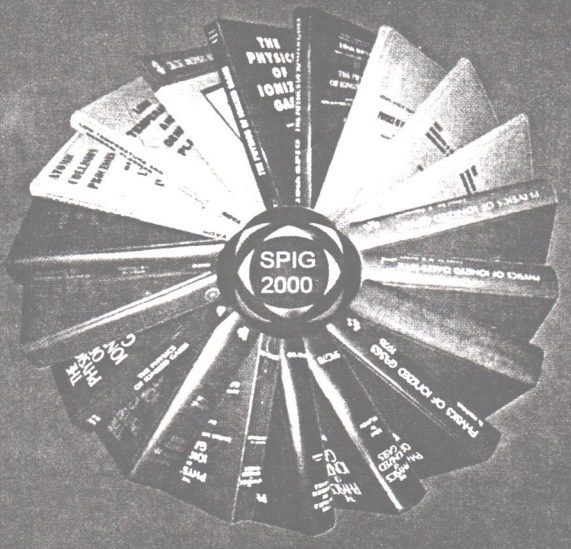

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COLLISIONS OF EXCITED ATOMS IN GAS DISCHARGES

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1. Introduction

Collisional processes involving excited atoms are an important factor in the kinetics of atmospheric and near-atmospheric discharges, which have attracted a renewed interest. These discharges are always partially ionized, with an electron energy distribution quite different from the local thermodynamic equilibrium. Extensive research has been conducted on the radiative properties of high pressure discharges and the development of new types of lasers and non-coherent light sources. Present work is inspired by the emerging attention to other physical properties of these discharges, which are less well understood. These are the interaction of high-pressure discharges with external electromagnetic fields, generation of internal electromagnetic effects closely related to the interaction of the discharges with acoustic waves, general aerodynamic properties, and the effects of chemical reactions on discharge parameters and kinetics.

This aspect of research can be exemplified by phenomena usually described as dispersion of acoustic shock waves in weakly ionized gas, as well as the related group of aerodynamic phenomena associated with strong, ionizing shock waves. The later were studied extensively in the 1960s and 1970s. After that period, the practical interest faded and only a few experiments on ionizing waves have been published since. However, many observations remained unexplained. For example, in neon excessive excited-states population was observed [1] in front of the ionizing shock wave. We have explained this observation by resonant radiation transfer across the shock structure and demonstrated the role of excited states in generating the combination of electromagnetic, kinetic, and aerodynamic effects in the shock region [2]. The phenomenon of ionizing shock wave is relatively simple and it was thought until the early '90s that all mechanisms of the wave were fully understood. An ionizing shock wave is a strong shock wave, generated in a laboratory shock tube at sub-atmospheric pressure. The wave propagates through the tube at supersonic speed (M=10-20) and carries enough energy to ionize the gas behind the

shock. The general assumption was that high pressure discharges exhibit, at least partially, some form of local thermodynamic equilibrium, and simplifications related to this assumption were usually used in the ionizing wave models. However, new observations [1] performed with updated spectroscopic tools and their interpretation based on currently available spectroscopic data, revealed additional features in the shock structure, suggesting a strong departure from equilibrium, especially in the regions close to the translational shock layer. Models based on local thermodynamic equilibrium were unable to explain the observation, and a reassessment [2] of the ionization-recombination process had to be made in order to analyze the experimental results. In many fast-changing situations the discharge conditions are far from equilibrium and the detailed description of ionization and recombination processes is necessary. The experimental result [1] was explained by introducing a detailed, nonequilibrium ionization-recombination model and by accounting for the radiative transfer of resonant lines across the shock structure. It was found that the dominant role in the ionization process was played by electron-impact ionization of excited states and by energy pooling ionization in collisions between two excited atoms.

The reason for our present interest in the ionization of excited atoms per se, is twofold: first, available data are very scarce; second, thermodynamic equilibrium conditions are not fulfilled. Therefore, implementing available data into an ionization-recombination model in a consistent manner proved to be a difficult task. Data were sparse and the implementation was sometimes ambiguous. This situation has not been a serious problem in modeling low pressure discharges, where processes involving excited atoms were less important [3-5]. However, at pressures above 10 Torr this is not the case. The relative contribution of individual elementary processes may differ substantially from the low-pressure discharge models, due to pressure and temperature dependence of rate coefficients and number densities of involved species.

In a gas discharge, excited atoms interact with photons, electrons, ions, and other ground state or excited atoms. In these interactions they may gain or lose energy, or may be transformed into ions. We are focused here on the processes leading to ionization of excited atoms. In gas discharges at elevated pressures ionization involves several competitive processes. These are electron-impact ionization from excited states,

ionization in collision between two excited states, associative ionization in three body processes involving a highly excited atom and two ground state atoms, and an atomic or molecular ion and two ground state atoms. This paper mainly covers the electron-impact and energy pooling ionization processes. Three-body ion conversion and homonuclear associative ionization processes are also important at higher pressures, but they require a separate treatment that is beyond the scope of this paper. Therefore, we will give only a few brief comments on these processes and for detailed information one should refer to reviews listed below.

Trajmar and Nickel [6] gave a comprehensive review of the work on electron impact by excited atom species. Lin and Anderson [7] have presented a review of the work on the electron excitation processes of rare-gas atoms. Siska [8] gave an extensive review of Penning ionization and energy-pooling processes. However, data on collisions involving excited atoms of the same species are still quite sparse. A review of the work on the subject before 1990 was given by Kolokolov and Blagoev [9]. Associative ionization was studied by Weiner *et al.* [10]. Smirnov [11,12] reviewed ion conversion, ion cluster growth, as well as homonuclear associative ionization processes. A review of collisional ionization of excited atoms, including the analysis of the homonuclear associative ionization process is given by Wuilleumier *et al.* [13].

2. Experimental Techniques for Collisions Involving Excited Atoms

There are considerable difficulties in measurements of collisions involving excited atoms because the atoms have to be produced, delivered to the interaction volume, and their population kept constant during the interaction. In the interaction region many channels of collisions are open and they are usually competitive. Therefore, detection techniques require careful calibration and data extraction procedure. As a consequence, the experiments are complex, expensive, and generate a limited amount of data. This, combined with the new, post-modern technical mentality of the users of these results, may be a partial explanation why so few experimental data actually exist.

The experimental techniques can be classified in four categories:

a) Crossed beam technique containing long-lived, metastable excited atoms,

b) *In situ* preparation of excited atoms in the interaction volume by photoexcitation,

c) Preparation of excited atoms by photoexcitation in a vapor cell, and

d) Monitoring excited state population and the analysis of the effects associated with a particular interaction of excited states in a glow discharge or its afterglow.

Crossed-beam experiments can only be applied to the studies of interactions between metastable atoms, since the finite time-of-flight from the source to the interaction region exceeds the lifetime of short-lived excited states. Metastable beams were generated mostly from noble gases due to the complications related to impurities in discharges with openly exposed electrodes. Attempts have been made to use electrodeless discharges, such as RF or microwave discharge to generate beams of other atoms, but the experimental data are still not available. Sources of metastable atoms can be further divided into low-energy sources and high-energy sources.

Low-energy (thermal) metastable beams are generated in devices that combine expansion through a nozzle and the source of excitation (discharge or electron beam impact source). The discharge is usually generated through the nozzle, and the arrangement resembles a flowing afterglow. Most frequently used types of discharge are the cold cathode d.c. glow discharge and the hollow cathode discharge, but radio-frequency and microwave discharges were also described in literature. Sources of metastable beams were reviewed in Refs. [6,8].

Thermal metastable beams cover the most interesting energy range for gas discharges, where the thermal kinetic energies of heavy particles are usually much lower than 1 eV. A typical nozzle expansion source based on a cold cathode d.c. glow discharge is described in Ref. [14]. This source was capable of generating a beam of a mixture of ground state and metastable atoms, where the target intensity of metastable fraction reached 10^{14}-10^{15} metastables/(s·sr). Beam energy range, defined by discharge conditions, nozzle characteristics, pressure difference, and target location, was typically 0.05 to 0.5 eV. The beam is far from being monoenergetic, since the discharge conditions dictated a wide kinetic energy range, close to the Maxwell-Boltzmann distribution.

High-energy beams of metastable atoms are generated in the charge exchange

process between a high energy noble gas ion beam and ground state alkali atoms, such as [15]

$$He^{+}(\approx 1keV) + Cs \rightarrow He^{*}(2^{1}S, 2^{3}S, \approx 1keV) + Cs^{+} \qquad (1)$$

The target density of helium metastable beam is about 10^5-10^6 metastables/cm^3 at beam energy of 1.6 keV.

Production of a short-lived excited state of sodium by photoexcitation was described in Refs. [16,17]. Ground-state atoms emerging from the atom-beam source were focused and partially velocity-and state-selected by a hexapole magnet and propagated to the interaction volume, where a laser beam at right angle intersected them. Photon energy of the laser beam was tuned to the sodium resonant transition. By comparison of signals in the detection plane with and without laser beams it was possible to determine quite accurately the fraction of the excited state fraction in the target region to be f=0.26 at the incident laser intensity of 120 mW/cm^2. This high excited-state fraction allowed accurate measurements of ionization cross section by measuring the ion current intensities after electron-atom collision with and without the laser beam and by monitoring the electron beam.

Associative ionization of excited alkali atoms was studied in vapor cell experiments, and the review of this work was given by Weiner *et al.* [10]. The alkali vapor was irradiated with a resonance lamp or a single-frequency laser tuned to near the alkali resonance. Associative ionization rate was the measured quantity, and the cross section had to be extracted by deconvolution, taking into account the velocity distribution of alkali atoms in the cell. In addition, the spatial distribution of excited alkali atoms in the cell, affected by resonant radiation trapping, inhomogeneity in the resonant absorption of incident photon beam, and by diffusion, had to be taken into account. Cross section data from cell experiments agree very well with the data from crossed-beam experiments [10].

Energy-pooling ionization data can be extracted by analyzing the electron energy distribution in the discharge afterglow. Kolokolov, Blagoev and coworkers [9,18,19] used this technique, which they named plasma electron spectroscopy, to extract the energy-pooling ionization rates in collisions of low-lying excited states of noble gases. They measured the electron energy distribution in the afterglow and compared the measured

distribution in the high energy tail with a distribution calculated from the Boltzmann equation, which did not contain the contribution of Penning electrons.

Okada and Sugawara [20] measured the decay rate of electron temperature in an argon afterglow. From the measured electron temperature and calculated energy gain of electrons from superelastic collisions and collisions between metastable atoms, they derived an average cross section for energy pooling ionization involving metastable argon atoms.

3. Ionization by Electron Impact

It has required considerable work to achieve convergence between experimental and theoretical results on ionization of excited atoms by electron impact. Most experimental data refer to an integral ionization cross section involving metastable targets [21]. The calculations of cross sections have still not achieved the desired level of accuracy. The Convergent Close-Coupling (CCC) calculations of ionization cross section [22] correctly describe the threshold behavior. However, CCC method tends to underestimate absolute values of ionization cross section at higher energies. In modeling, the most frequently used data are based on simplified empirical or semi-empirical formulae, such as [23,24]:

$$\sigma(e) = \frac{6.5\times10^{-14}}{E+\alpha E_i}\left(\frac{5}{3E_i}-\frac{1}{E}-\frac{2E_i}{3E^2}\right) \qquad (2)$$

where E and E_i are the incident energy of the electron and the ionization energy of the excited state, respectively, given in eV, α is the adjustable constant usually taken as α=2 near the threshold, and α=3.25 at higher energies, and σ(E) is given in cm^2. This formula tends to overestimate cross sections close to the threshold but agrees better with experimental data at higher energies.

Our measurements of electron impact ionization of laser-excited sodium 3P state [25], and the experiment of Trajmar *et al.* [26] on barium, still remain the only ionization measurements on short-lived excited states. We measured the absolute cross sections in the incident electron energy range from threshold to 30 eV for both excited and ground state sodium. Excited-state results are given in Fig. 1(a) together with calculations [22-24,27]. It can be seen that the results of the CCC calculation tend to

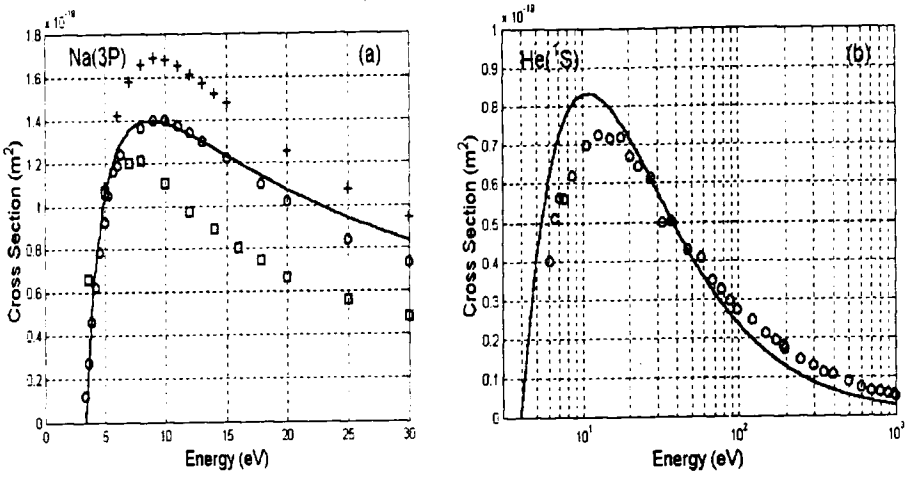

Fig. 1. Electron impact ionization cross section as a function of electron energy.
Fig. 1(a). Na(3P): circle, Tan at al. [25]; full line, Vriens [23]; cross, McGuire [27]; square, Bray [22].
Fig. 1(b). He(2^1S): circle, Dixon et al. [21]; full line, Vriens [23].

agree with experiment near threshold, but remain below experimental data at higher energies. On the other hand, the calculations employing generalized oscillator strength (GOS) based on the Born approximation [27] tend to underestimate cross sections near the threshold, but agree better with experimental data at higher energies. Position of the maximum is close to the one predicted by the GOS calculation, while the CCC treatment underestimates the energy at the maximum by 3 eV. However, the semi-empirical Eq. (2) agrees surprisingly well with the experiment, much better than the two, more elaborate calculations. Fig. 1(b) presents a comparison of experimental data for metastable helium (He 2^1S) and the ionization cross section calculated using the Eq. (2). The formula overestimates the cross section around threshold and maximum, and agrees rather well with the experimental results at higher energies.

4. Energy - Pooling Process

Ionization in a collision involving two excited states has two types of ion products:

$$A^* + A^* \xrightarrow{k_{ee}} A^+ + A + e^- (\Delta E) \qquad (3a)$$

$$A^* + A^* \xrightarrow{k_M} A_2^+ + e^- (\Delta E) \qquad (3b)$$

where k_{EP} and k_{AI} are the rate coefficient for energy pooling (atomic ion production) and for associative ionization (molecular ion production), respectively. In both ionization channels, the ejected electrons carry out most of the excess kinetic energy. These features of the process contribute to the recovering of the excited state population and affect the electron energy distribution in the discharge. However, this aspect of the energy pooling process has usually been neglected in most models of gas discharges. Since the process depends predominantly on the long range van der Waals attraction forces, the polarized excited states have a much lower collision probability than the unpolarized states. The fact that polarized excited state can affect ionization has been used in cold collision physics with attempts to create BEC out of excited neon atoms [28].

Experimental data on energy-pooling processes are sparse, but there is no justification for using arbitrary values for rate coefficients in the models of gas discharge. With the aim to overcome this situation we will present here three kinds of data: experimental, analytical based on exact theories involving *ab initio* calculation of the potential and autoionization shift curves [29], and approximate analytical data, based on a simplified orbiting collision model [30]. With the knowledge of ion potential curves, one can also determine the cross section for the associative ionization. However, it was shown for helium that the orbiting method grossly overestimates the contribution of associative ionization in the total ionization cross section [29].

Available data on the collision of two lowest-energy metastable helium atoms He(^{3}S) allow comparison of all three types of data. The orbiting model reduces the problem of the collision cross section calculation to the attractive van der Waals potential between two excited atoms. Therefore the approximate analytical data based on the orbiting model are generated in the following steps:

a) calculate dipole polarizability of each particular excited state based on compiled data on oscillator strengths,

b) evaluate approximate van der Waals constant C_6,

c) evaluate total ionization cross section using the orbiting model, and

d) evaluate total ionization rate by averaging over the excited atom velocity distribution function.

Dipole polarizabilities were calculated using the expression in terms of the dipole oscillator strength distribution [31,32]

$$\alpha_0(k) = \frac{e^2}{m_e}\left[\sum_{l'\neq k}\frac{f_{kl'}}{\omega_{kl'}^2} + \frac{1-\sum_{l'\neq k}\frac{f_{kl'}}{\omega_{kl'}^2}}{2\omega_{\min}^2}\right] \tag{4}$$

where e and m_e are the electric charge and the mass of an electron, respectively; $f_{kl'}$ is the oscillator strength for transition between a state l' and the state k; $\omega_{kl'}$ is the frequency difference; ω_{min} is the smallest possible energy difference; the summation is taken over all levels with known oscillator strengths for transition to state k; and an arithmetic mean was taken between the lower bound (first term only) and the upper bound of the dipole polarizability.

With calculated dipole polarizabilities, the van der Waals constant C_6 was evaluated using the Slater-Kirkwood approximation

$$C_6^{AB} \approx -\frac{3}{2}\sqrt{\frac{e^2\hbar^2}{m_e}}\frac{\alpha^A\alpha^B}{\sqrt{\alpha^A}+\sqrt{\alpha^B}}. \tag{5}$$

Total ionization cross section can be then estimated based on the assumption that the autoionization of the intermediary molecular excited state can occur if, and only if, the collision energy E is greater than the relative maximum in the effective radial potential. The total ionization cross section σ_{tot} is given by [29]

$$\sigma_{tot}(E) = \pi R^2\left[1-\frac{V_0(R)}{E}\right]; \quad V_0(R) = -\frac{C_6}{R^6} \tag{6}$$

where $R=R(E)$ is the larger root of the equation

$$E = V_0(R) + \frac{1}{2}RV_0'(R) \tag{7}$$

where $V_0'(R)$ is the derivative of V_0 over interatomic distance.

Finally, the ionization collision rate can be calculated from

$$k_{EP} = \int_0^\infty \sigma_{tot}(E)vf(E)dE \tag{8}$$

where v is the relative velocity of two excited atoms. In the approximation of thermal equilibrium between heavy particles, $f(E)$ is the Maxwell-Boltzmann distribution and the ionization rate is proportional to [4, 33]

$$k_{EP} \approx const \times C_6^{1/3} T^{1/6} m^{-1/2} \tag{9}$$

where T is gas temperature in the discharge and m is the mass of excited atoms.

In Fig. 2(a) are shown the total cross sections for energy pooling ionization in the collision of two ^{3}S states, obtained using the exact theory of autoionization of the intermediary state and the approximate orbiting model as outlined above. It can be seen that the two results do not differ substantially in the most important energy range, between 0.01 and 0.3 eV. Also shown are several experimental results given in terms of cross section [6, 34-37]. Results from Refs. [34] and [37] agree rather well with calculations.

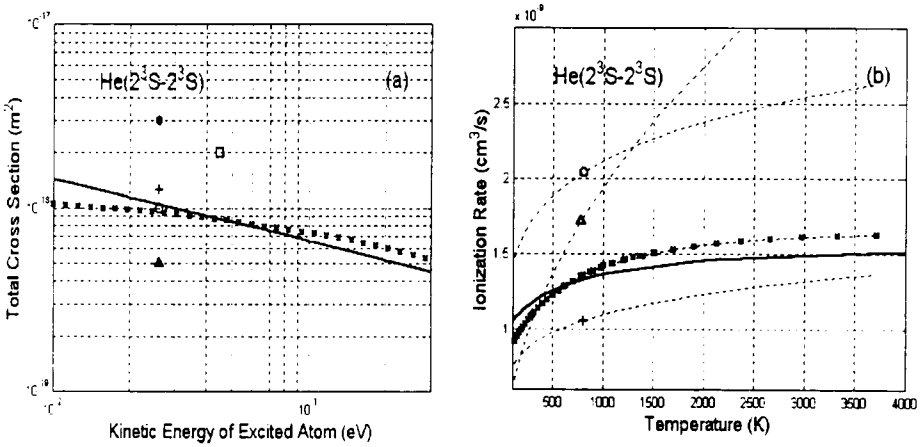

Fig. 2. Energy pooling results.

Fig 2(a). Energy pooling ionization cross section as a function of kinetic energy of excited atom: full line, present data; xxx, Garrison et al. [29]; triangle, Kolokolov and Blagoev [9]; circle, Phelps and Molnar [34]; square, Hurt [35]; hexagram, Johnson and Gerardo [36]; cross, Deloche et al. [37].

Fig 2(b). Energy pooling ionization rate as a function of temperature: full line, present data; xxx, Garrison et al. [29]; dash line marked by cross, Kolokolov and Blagoev [9]; dash line marked by circle, Bates et al. [30]; dash line marked by triangle, frequently used assumption $k=\langle v\rangle\sigma(300\ K)$.

In Fig. 2(b) we show the ionization rate for the energy pooling process between two He(^{3}S) metastable atoms, based on the cross section data from Fig. 2(a) and on the

Maxwell-Boltzmann velocity distribution of excited atoms. Comparison includes ionization rates calculated from the cross sections evaluated in Ref. [29] which we will label "exact theory", ionization rates calculated by Bates *et al.* [30] with the orbiting model, ionization rates calculated by Kolokolov and Blagoev [9], present calculation, as well as the ionization rate evaluated on the basis of the frequently used assumption of constant cross section. The ionization rate has a relatively weak dependence on temperature, since the decreasing energy dependence of the cross section compensates the temperature dependence of the velocity distribution.

Most estimates of energy pooling ionization rates in the gas discharge models assume a constant cross section over the relevant energy range. As shown on Fig. 2(b), this assumption can produce an error of more than a factor of two. Moreover, the ionization rate has usually been taken as 2×10^{-9} cm^3s^{-1} over the whole gas temperature range. This assumption can produce an error between 25% and 75%. Therefore, in the cases where a relatively wide gas temperature range is expected, as in high pressure discharges, these crude approximations may produce substantial error. As seen from the Fig. 3b, the orbiting model formula derived by Bates *et al.* [30] overestimates, while Kolokolov and Blagoev [9] underestimate the ionization rate in comparison to the present calculation. Experimental values for ionization rates differ substantially, and we tend to believe that the measured quantity is an average over all excited states. Therefore, most of the experimental values are larger than the ionization rates for the lowest lying states. On the other hand, the method used by Kolokolov *et al.* [9, 18, 19] has the capability of discriminating between the higher excited states. Their experimental values tend to be lower than the calculated values. On the calculation side, it is known that the Slater-Kirkwood relation tends to underestimate the van der Waals constant, which leads to lower values of cross sections and ionization rates. Clearly, further work on clarifying these discrepancies is needed.

The above values of ionization rates hold for the lowest lying metastable state of helium. The singlet state $He(^1S)$ reacts with 2.5 times larger ionization rates. A calculation of ionization rates for higher excited states at extremely low temperatures of cold collisions suggest that rates increase by up to an order of magnitude [28]. At higher

temperatures, the same method of calculation is difficult to use. Besides, this calculation requires exact knowledge of molecular potentials, which are not always available.

Based on the results shown in Figs. 2(a) and 2(b) for excited helium, we proceed applying the above approximation to calculate the ionization collision rates of other excited noble gas atoms. There are almost no experimental data for cross sections and ionization rates of gases other than helium. Although one should not expect a surprise, the experimental verification of the theory is always favorable, especially in cases when the only two available data points differ by a factor of three or more.

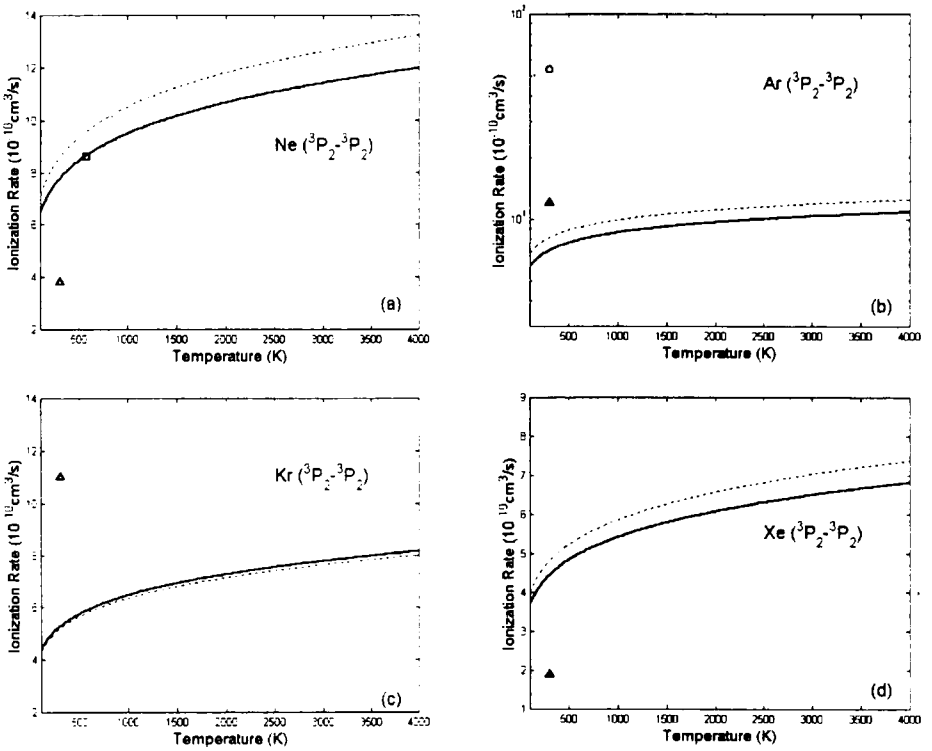

Fig. 3. Ionization rate as a function of temperature for Neon (a), Argon (b), Krypton (c), and Xenon (d): full line, present data; dash line, Kolokolov and Blagoev [9] calculation; triangle, Kolokolov and Blagoev [9] experiment; square, Salinger and Rowe [38]; circle, Okada and Sugawara [20].

Energy pooling ionization rate for a collision between two metastable Ne($^3P_2$) states is given in Fig. 3(a). The discrepancy between present calculation and Ref. [9], as well as the result obtained by Salinger and Rowe [38] at T = 573 K can be attributed to

the uncertainty in the oscillator strength data used in each calculation. The experimental results from Ref. [9], obtained with the plasma electron spectroscopy technique in a discharge afterglow at T = 300 K are smaller than calculated values by a factor of two. In the of case of argon [Fig. 3(b)], the positions of two experimental results at T = 300 K, obtained with two different techniques, plasma electron spectroscopy [9] and electron temperature decay [20], are above the calculated ionization rates. However, the experimental result of Ref. [20] is larger by a factor of 4.5 than the result in Ref. [9]. Ionization rates for Krypton and Xenon metastable states are given in Figs. 3(c) and 3(d), respectively. Experimental result for Krypton at 300 K is a factor of two larger than the calculated value. On the other hand, the experimental result for Xenon at 300 K is a factor of 2.3 smaller. Both results were obtained by plasma electron spectroscopy [9] and were given with error bars substantially smaller than the difference from the calculated values at 300 K.

The approximate character of the Slater-Kirkwood relation, which tends to underestimate the van der Waals interaction constant, can partially explain the large discrepancies between calculation and experiment. Further, the dynamics of the intermediary excited complex in the ionization process is unknown and the uncertainties about the spin conservation rule in its decay may lead to additional error in calculation. Finally, the uncertainties in oscillator strength data may also contribute to the error.

On the experimental side, it is not clear how the contribution of higher lying states affects the extraction of energy pooling ionization cross section from electron temperature decay [20]. Plasma electron spectroscopy [9] has more capability to discriminate between the excited states. However, both procedures are complex and the uncertainties in the extraction procedure may be large.

Having in mind large uncertainties and an insufficient amount of reliable experimental data, the suggested values of the energy-pooling ionization rates involving the lowest metastable state are given in Fig. 4. They are based on the simplified calculations using the orbiting model and the Slater-Kirkwood relation. Therefore they tend to underestimate the ionization rates. However, except partially for Kr and Xe, they are substantially larger than the constant value usually used in modeling the discharges at low pressures (see, for instance Refs. [3-5]).

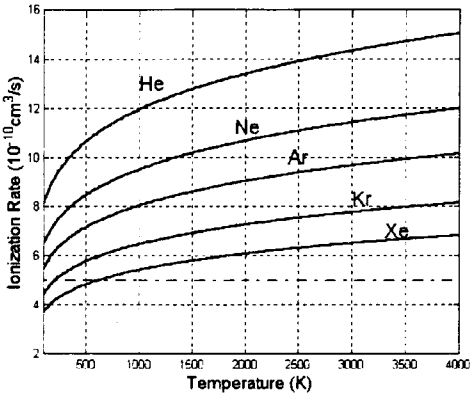

Fig. 4. The energy-pooling ionization rates involving the lowest metastable state of noble atoms as a function of temperature: full line, the suggested value for indicated noble atom; dash-dot line, most frequently used value for all noble atoms.

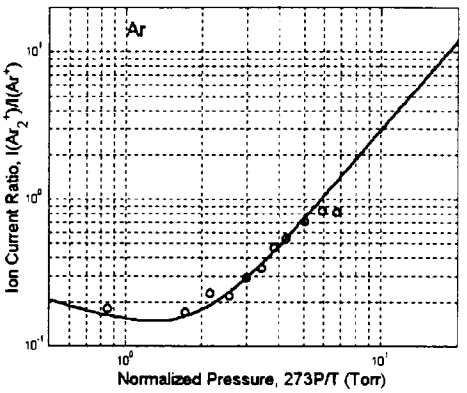

Fig. 5. Ratio of molecular ion current [$I(Ar_2^+)$] and atomic ion current [$I(Ar^+)$] as a function of normalized pressure: circle, Gaur and Chanin [43]; full line, fitted data.

5. Associative Ionization Processes

Associative ionization processes include, besides the second channel in the collision between excited atoms [Eq. (3b)], the associative ionization in collision of an excited atom with a ground state atom

$$A^{**} + A \rightarrow A_2^+ + e^- \qquad (10)$$

The two processes, (3b) and (10), are also called homonuclear associative ionization. Termolecular (three bodies) associative ionization or ion cluster growth is defined as

$$A_n^+ + A + A \rightarrow A_{n+1}^+ + A\,, \quad n>1. \qquad (11)$$

The three reactions are responsible for production of molecular ions. They are of minor importance in gas discharges at low pressures, but at high pressures and low temperatures, they can become a dominant ionization mechanism.

Weiner *et al.* [10] have discussed the process of associative ionization between two Na($3p\ ^2P_{3/2}$) atoms in different experimental devices. In cell experiments (~450 K) the associative ionization cross section was 7.3×10^{-16} cm^2 and in the crossed-beam-experiments at $v = 10^5$ m/s the cross section was 8.9×10^{-16} cm^2 [30,40]. Cross section

measured in the optical trap at 0.75 mK was larger by three orders of magnitude [10]. Calculation of partial cross sections in this type of collisions is rather complex. Simple models, such as the orbital model, strongly overestimate the associative ionization cross section [29].

Although the failure of semiclassical theories to describe homonuclear associative ionization (HMI) were discussed in a few examples in a review by Weiner *et al.* [10], some qualitative information can be derived from the simple treatment outlined by Smirnov [11]. Following Smirnov the ionization rate is proportional to

$$k_{HMI} \sim T \times e^{-\frac{U(R)}{kT}} \tag{12}$$

where U(R) is the interaction potential between the incident atoms at minimal internuclear distance in the collision.

The ionization rate has a maximum at certain principal quantum number. This was correctly predicted by the theory of Janev and Mihajlov [41]. The principal quantum number for maximum ionization rate depends on temperature as $n \sim I/\not\in T$ [11]. Therefore, at elevated temperature in gas discharges the position of the maximum may shift toward lower lying excited states leading to the decreasing affect of highly excited states.

Termolecular associative ionization (TAI) is a relatively well known process [11]. It seems that a simple power relationship $k_{TAI} \sim T^{-n}$ is an accurate description in argon for the decrease of rate coefficient with heavy-particle temperature. As outlined in Ref. [11] a simple estimate, based on the polarization interaction only, suggests n=0.75. However, Hamon *et al.* [42] derived an empirical relation based on several experiments performed in a wide temperature range, which gives n=1.05. This result suggests that the exchange interaction play a certain role in this process. Extrapolating these trends to the gas temperature range which is characteristic for gas discharges, indicates a factor of two discrepancy between the simple estimate [11] and empirical data [42-44]. Therefore, the following relation can express the ionization rate for termolecular associative ionization in argon

$$k_{AI} = 2.4 \times 10^{-31} \left(\frac{T}{300} \right)^{-1.05} cm^6 s^{-1} \tag{13}$$

It is interesting to note that the relative contribution of molecular ions in the overall population of heavy charged particles tends to increase rapidly after a certain

pressure is reached at a given temperature. This is shown in Fig. 5, where the ratio of molecular and atomic ion current in an argon discharge is plotted against the normalized pressure, (273×p)/T [43]. There is a sharp distinction between the "low pressure" region, were the contribution of molecular current is low, and "high pressure" region, were molecular component becomes dominant.

6. Conclusion

Studies of gas discharges at elevated pressures (above 10 Torr) are presently faced with a paradox. The importance of collisions involving excited atoms and molecules is obvious, yet very few data are available. This paper outlined some of the problems, which are encountered in the studies of gas discharges at elevated pressures. We have illustrated the present situation with an analysis of ionization processes. At low pressures, the ambiguity in the quantitative description of ionization processes is of minor relevance. At elevated pressures there are discharge conditions where excited states are important population and could have the dominating influence on ion composition. In particular, the discrepancy between calculated and measured rate coefficients for energy-pooling processes was discussed. Clearly, the refinement of both the experimental work and calculations is needed to obtain a satisfactory level of information on these processes. The information on processes involving highly excited states is almost nonexistent, and their contribution to the ionization-recombination process could not be correctly accounted for at the time of this writing.

The scope of this review did not allow for an in depth analysis of associative ionization processes, nor a complete overview of the available information on these processes. However, we hope the analysis presented will be an encouragement to other researchers to consider and study in more detail the collisions involving excited atoms.

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