Chemi-ionization in neon plasma

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The density of electrons formed in binary collisions of $2p^5 3s$ neon atoms was measured in the afterglow of a low pressure glow discharge by observing the high energy tail of the electron energy distribution function (EEDF) using a Langmuir probe. In the afterglow, the bulk plasma electrons thermalize but the density of $2p^5 3s$ neon atoms remains significant. In an ionizing collision, a pair of these atoms releases high energy (~11.6 eV) electrons which form a characteristic peak in the EEDF. Simultaneously with the chemi-ionization electrons, the densities of $1s_2$, $1s_3$, $1s_4$, and $1s_5$ neon atoms were independently measured using diode laser absorption spectroscopy. It was found that the data obtained are described well by a single chemi-ionization reaction when the $2p^5 3s$ configuration is considered a single state. The corresponding rate coefficient, found to be $(3.2 \pm 0.4) \times 10^{-10}$ $\mathrm{cm}^3\,\mathrm{s}^{-1}$ at a temperature of 310 K, is recommended for use in discharge modeling.
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INTRODUCTION

Of the rich variety of inelastic collisions between excited atoms, those resulting in the formation of atomic or molecular ions (chemi-ionization) play a unique role in discharge plasmas. In an initial phase of the development of the discharge, these processes account for more than 80% of all ionization events in the plasma.[1] Chemi-ionization involving low-lying metastable states is also a dominant ionization mechanism in a decaying plasma.[2] Modeling of nonequilibrium plasmas, in particular those used in light sources, is increasingly important in predicting device performance and determination of optimal regimes for their operation. Good knowledge of the elementary processes is a prerequisite for any such model. Rare gas discharges, traditionally considered poor candidates for lighting applications have recently been the subject of renewed interest. For example, neon lamps are used for some automobile applications, in which the red visible lines may be used directly for stop signals,[3] or combined with radiation converted from the violet UV (VUV) by a green phosphor to provide an amber light for other traffic signals.[4] In certain discharge regimes, values of rate coefficients of chemi-ionization processes that involve collisions of the excited neon atoms significantly affect model predictions.[2] These processes, however, are poorly studied and quantitative data on the rate coefficients are scarce.

The low $2p^5 3s$ neon states ($1s_5$, $1s_4$, $1s_3$, and $1s_2$ in Paschen notation) are significantly populated in a discharge. A binary collision between these atoms may result in the formation of an atomic or molecular ion and a fast (~11 eV) electron, according to following reaction:

$$\mathrm{Ne}(1s_{5,4,3,2}) + \mathrm{Ne}(1s_{5,4,3,2}) \rightarrow \begin{array}{l} \mathrm{Ne} + \mathrm{Ne}^+ + e \\ \mathrm{Ne}_2^+ + e \end{array}. \tag{1}$$

Rate coefficients for these reactions may be obtained by counting the number of fast electrons produced by chemi-ionization (referred to below as chemi-ionization electrons) and measuring the populations of the excited states involved in the collision. In the afterglow phase of the discharge, when the bulk plasma electrons thermalize but the density of $2p^5 3s$ neon atoms remains significant, the high energy (>10 eV) electrons in the plasma are those produced through chemi-ionization and in superelastic collisions of electrons with excited neon atoms. The latter have a different energy than chemi-ionization electrons, therefore the number of electrons formed through reaction (1) in the plasma may be obtained by measuring a corresponding region of the electron energy distribution function (EEDF) using a Langmuir probe. This method, known as plasma electron spectroscopy, is described in detail elsewhere.[5] For a glow discharge formed in a cylindrical tube, with a probe placed on the tube axis, the chemi-ionization electron density, n_c, is

$$n_c \approx \sum_{i,j=2}^{5} \xi_{ij} k_{ij} \frac{\langle n_i n_j \rangle r_0^2}{\mu_1^2 D(11.6\mathrm{eV})}. \tag{2}$$

Here $D(\varepsilon)$ is the diffusion coefficient for an electron with energy ε; r_0 is the tube radius; μ_1 is the first root of zero-order Bessel function $J_0(x)$; $\langle n_i n_j \rangle$ is the product of the excited atom densities averaged over the tube diameter; and k_{ij} is the corresponding rate coefficient. Subscripts i and j denote specific states involved in the collision, and the factor ξ_{ij} is introduced to distinguish between symmetric and asymmetric collisions: $\xi_{ij}=1$ when $i \neq j$, and $\xi_{ij}=1/2$ when $i=j$. An experimental value for n_c is found by integrating the measured EEDF over the expected energy range for chemi-ionization electrons:

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$$n_c = \int_{\Delta 11\text{eV}} f(\varepsilon) \frac{4\pi\sqrt{2\varepsilon}}{m^{3/2}} d\varepsilon. \quad (3)$$

Here $f(\varepsilon)$ is the EEDF measured on the discharge axis; m and ε are the electron mass and energy in eV, respectively. According to Druyvesteyn's formula,[5] the EEDF can be expressed in terms of the second derivative of the electron current to the probe with respect to the probe potential, $\partial^2 i_e / \partial u^2$:

$$f(\varepsilon) = \frac{m^2}{2\pi A e^3} \frac{\partial^2 i_e}{\partial u^2}, \quad (4)$$

where e is the electron charge, and A is the probe area.

EXPERIMENT

The experiments were conducted in a decaying plasma at a neon pressure of 1.3 Torr (measured at 25 °C). In different series of experiments, 40 and 100 μs rectangular-shaped voltage pulses were applied to the electrodes of a U-shaped cylindrical glass discharge cell with an inner diameter of 28 mm, total length of 25 cm, and horizontal section length of 10 cm. In each series of experiments, the discharge current was varied from 10 to 150 mA, and the discharge repetition frequency was kept 1 kHz throughout the experiment. To measure the EEDF, a tungsten wire probe, 0.1 mm in diameter and 10.7 mm long, was placed along the discharge cell axis. The measurements were taken in the afterglow, delayed from 50 to 150 μs beyond the end of the excitation pulse. The experiment was controlled by a host computer and an associated electronic circuit developed in the laboratory. The circuit generated control pulses for the high voltage power supply to drive the discharge, ramped the probe electric potential and sampled the probe current in the discharge afterglow at selected time intervals. In addition, the circuit generated triggering pulses for optical measurements. An example of the EEDF measured in the experiment is presented in Fig. 1.

Radial profiles for the *1s* neon atom densities were measured using diode laser absorption spectroscopy. An external cavity diode laser, a product of Environmental Optical Sensors Inc, was employed. The laser wavelength was tuned to a selected transition (see Table I) and the attenuation of the beam by a 10 cm plasma column was measured. Using two laser diodes, with center wavelengths of 655 and 635 nm, respectively, absorption spectra for each of the transitions listed in Table I were recorded. A typical spectrum is shown in Fig. 2. The spectra were obtained by scanning the diode laser frequency in 30 or 60 MHz increments through the absorption line of interest. The instability of the laser frequency did not exceed 4 MHz in the experiments. By fitting experimental data with a model function, a combination of Voigt line shapes for neon-20 and neon-22 isotopes, provided a measurement of excited state densities for each isotope. Oscillator strengths were taken from Ref. 6. The laser beam was displaced parallel to the tube axis so that radial density profiles could be recorded. It was found that the experimental dependences are satisfactorily described by the zero order Bessel function of first kind: $n_i(r) = n_i(0) J_0(\mu_1 r / r_0)$. This approximation was further used in chemi-ionization rate coefficient calculations [see Eq. (2)].

Results for the excited state and the chemi-ionization electron density measurements are compiled in Table II.

TABLE I. Optical transitions used in the absorption measurements.

State	Transition	Wavelength (nm)	Oscillator strength[a]
$1s_2$	$1s_2 \rightarrow 2p_2$	659.9	0.164
$1s_3$	$1s_3 \rightarrow 2p_7$	653.3	0.246
$1s_4$	$1s_4 \rightarrow 2p_7$	638.3	0.170
$1s_5$	$1s_5 \rightarrow 2p_8$	633.4	0.0818

[a]Reference 6.

DISCUSSION

The second derivative of the probe current was calculated using three measurements of the current: $i(u\text{-}\Delta u)$, $i(u)$, $i(u+\Delta u)$ where Δu is a probe potential ramping increment. For a measurement to be useful, the difference $[i(u\text{-}\Delta u) - 2i(u) + i(u+\Delta u)]$ should be greater than the noise currents of the measurement circuit and plasma. Therefore, at a given noise level, an appropriate

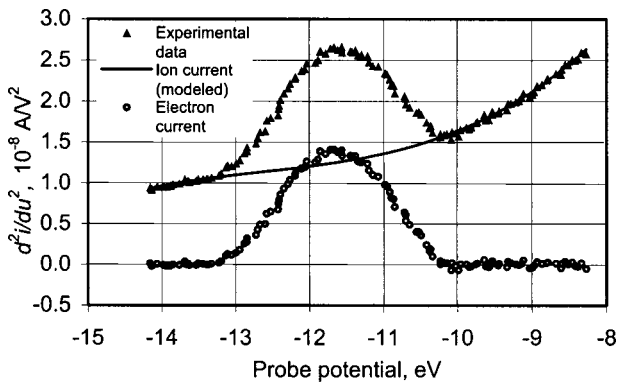

FIG. 1. High-energy part of the second derivative of the probe current. Neon pressure of 1.3 Torr. Discharge current of 20 mA, duration of 100 μs, and afterglow delay of 80 μs. The EEDF is calculated using Eq. (4).

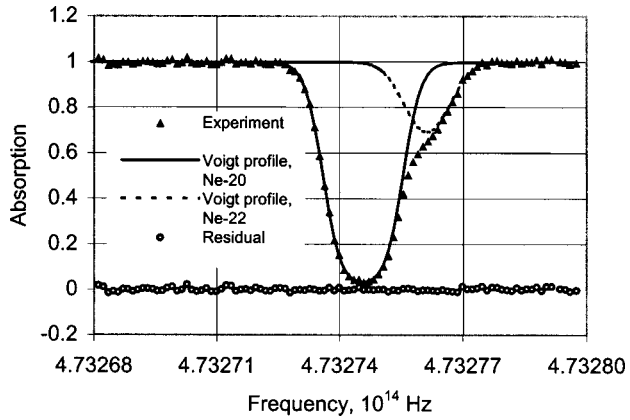

FIG. 2. Absorption spectrum for transition $1s_5 \rightarrow 2p_8$ (the center wavelength is at 633.443 nm). Neon pressure of 1.3 Torr, discharge current of 10 mA, duration 100 μs, and afterglow delay of 100 μs.

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TABLE II. Neon excited state and chemi-ionization electron densities.

Discharge duration (μs)	Measurement delay (μs)	Discharge current (mA)	Combined neon-20 and neon-22 density at the tube axis (10^{10} cm^{-3})				Electron density (10^5 cm^{-3})
			$1s_5$	$1s_4$	$1s_3$	$1s_2$	
100	50	10	25.6	6.0	2.7	0.28	7.9
100	100	10	23.2	3.3	2.4	0.07	5.7
100	150	10	22.9	2.4	2.1	0.08	5.3
100	50	20	30.6	8.8	3.2	0.50	9.6
100	80	20	34.4	6.5	3.5	0.25	9.9
100	150	20	28.0	3.9	2.3	0.09	6.2
100	50	35	37.0	12.7	4.1	0.66	15.5
100	100	35	34.0	8.0	3.4	0.30	11.5
100	150	35	21.7	4.1	1.6	0.11	5.1
100	50	50	44.0	14.5	5.0	1.00	25.9
100	150	50	29.8	6.5	2.0	0.16	8.5
40	150	50	23.0	4.3	1.8	0.12	2.2
40	50	100	28.9	11.0	3.6	1.43	10.8
40	100	150	31.2	10.4	3.1	0.69	12.6

value of the ramping increment Δu should be chosen. In our experiment, the current noise was at a level of 100 nA, corresponding to a minimum Δu of 1 volt (cf. Fig. 1). This a resolution allows unambiguous separation of the electrons formed in the course of reaction (1) from the bulk plasma electrons or fast electrons formed in other chemi-ionization reactions or in super-elastic collisions. However this resolution is insufficient to separate contributions to the chemi-ionization electron current made by each specific pair of excited states in the $2p^5s$ configuration. There is a total of 10 possible channels for reaction (1), with expected energies of the chemi-ionization electron ranging from 11.67 to 12.14 eV. Contributions from each of the possible channels to the measured electron density depend on the specific chemi-ionization rate coefficient (k_{ij}) and excited state populations [n_i and n_j; see Eq. (2)]. By varying discharge conditions such as discharge current and duration, measurement delay, and gas pressure, and measuring the chemi-ionization and excited state populations, one may attempt to extract the rate coefficients using variational methods. For a 10-dimensional problem, with a measurement uncertainty of 10%, however, it would require a large number of measurement points to evaluate the rate coefficients to acceptable precision, assuming that the excited state populations do not correlate with each other. Certain assumptions could be applied to simplify the problem. In two previous works where the chemi-ionization electron density was measured in neon afterglow,[7,8] it was concluded that only the lowest $1s_5$ and $1s_4$ neon states contribute to the chemi-ionization electron current. Blagoev and Popov[7] also neglected the contribution from binary collisions of $1s_4$ atoms, while Demidov and Kolokolov[8] obtained a very small value for k_{35} after fitting their experimental data to the model function Eq. (2). Both teams reported two rate coefficients: those for binary collisions of two metastable $1s_5$ states (3.7×10^{-10} and 3.8×10^{-10} cm^3 s^{-1}), and those for a collision between the metastable $1s_5$ and radiative $1s_4$ states (3.5×10^{-9} and 1.4×10^{-9} cm^3 s^{-1}, in Refs. 7 and 8, respectively). Neither team accounted for symmetry of the $1s_5-1s_5$ collision [i.e., the fact that $\xi_{55}=\frac{1}{2}$ in Eq. (2)], therefore the reported rate coefficients for this reaction should be increased by factor of 2, leading to $k_{55}=7.4\times10^{-10}$ cm^3 s^{-1} in Ref. 7 and $k_{55}=7.6\times10^{-10}$ cm^3 s^{-1} in Ref. 8. The small number of dissimilar measurements (five in experiment in Ref. 7 and four in experiment in Ref. 8) leads to a strong dependence of the solution for coefficient k_{45} on the electron and atom density fluctuations. This may be the reason for the significant difference between coefficients k_{45} and k_{55} reported by both teams, and for the discrepancy between coefficient k_{45} reported in Refs. 7 and 8, respectively.

Modern theoretical descriptions of chemi-ionization in collisions between excited atoms[9] indicate that the contribution of $1s_4$, $1s_3$ and $1s_2$ states to the chemi-ionization current may be considered negligible when populations of these states are at least an order of magnitude less that that of the $1s_5$ state. Analysis of the data presented in Table II does not provide sufficient grounds for such an assumption. In addition, the populations of metastable states ($1s_3$ and $1s_5$) exhibit a strong correlation over the entire range of experimental parameters, therefore contributions of these states to the chemi-ionization current cannot be separated even for a large number of dissimilar measurements.

An alternative approach is to consider configuration $2p^53s$ a single state. Then, the observed chemi-ionization current is described by a single reaction and

$$n_c=\tfrac{1}{2}k_{eff}\frac{<n^2>r_0^2}{\mu_1^2 D(11.6eV)},$$

where $n=\Sigma_{i=2}^{5}n_i$. Calculated under this assumption, the rate coefficient, $k_{\text{eff}}=(3.2\pm0.4)\times10^{-10}$ cm^3 s^{-1}, is found to be independent of the plasma conditions (Fig. 3) and therefore can be used as an atomic constant in modeling. The gas temperature at the plasma axis, retrieved from absorption profiles, was 310 K. The main sources of error for the rate coefficient are the uncertainties in electron and excited neon density measurements. The uncertainties of individual measurements are illustrated in Fig. 3 by error bars. Using data available in Refs. 7 and 8 we calculated the effective rate coefficients for those experiments, $k_{\text{eff}}=1.7\times10^{-9}$ and k_{eff}

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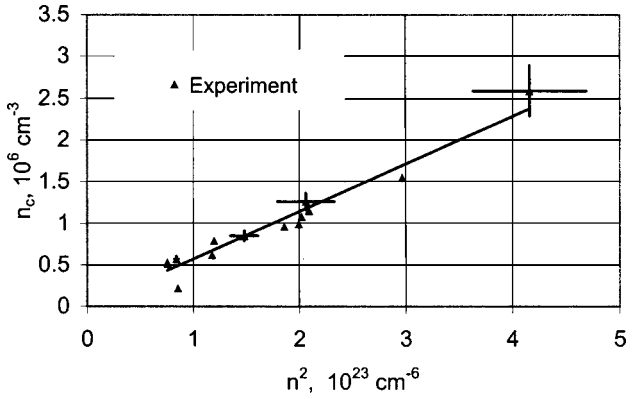

FIG. 3. Density of chemi-ionization electrons vs the squared combined density of $1s_2$, $1s_3$, $1s_4$, and $1s_5$ states.

$=1.6\times10^{-9}$ cm^3 s^{-1}, respectively. The reason for a significant discrepancy between these coefficients and the present measurements is related to the difference in density of the upper $1s_3$ and $1s_4$ states measured in this experiment and measured or estimated in experiments.[7,8] The excited state densities were obtained in Refs. 7 and 8 using a variation of the absorption method that involved two identical discharge cells. This method is very sensitive to changes in both the light source emission and the experimental cell absorption line profiles which were not measured in these experiments.

The rate coefficients for de-excitation of the $1s_5$ state in symmetric collisions were also reported in Ref. 10: $k_{55}=2.0\times10^{-9}$ cm^3 s^{-1} and, earlier, in Ref. 1: $k_{33}\approx k_{35}\approx k_{55}=0.8\times10^{-9}$ cm^3 s^{-1}. These coefficients were deduced from the temporal and pressure dependencies of the excited state densities[10] and discharge parameters[1]. While the dependencies observed in these experiments could be interpreted as a strong indication that the losses of excited atoms are nonlinear with respect to their densities, the deduction of specific rate coefficients is heavily reliant on the characteristics of the model used to describe the observed dependencies. Such indirect measurements usually are burdened with a number of assumptions, and sometimes are controversial. For example, in Ref. 10, the authors simplified the model for low discharge currents (around 1 mA) by neglecting the chemi-ionization term in the excited state density balance equations, apparently to deduce rate coefficients for other processes, such as depopulation of the state by electron impact. In the second stage of their analysis, for higher discharge currents, they include the chemi-ionization term and deduce its rate coefficient, which happened to be a rather high value. Returning to the low current measurements, one finds that the loss due to chemi-ionization is no less than that due to electron impact, therefore the initial assumption was not correct. Overall, uncertainties for rate coefficients found by fitting procedures are determined mostly by the accuracy of the model and other coefficients used in the procedure which are rather hard to evaluate. Experiments in which the input and the output of the reaction under study are directly measured should be considered a preferable source for atomic data.

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[1] S. N. Salinger and J. E. Rowe, J. Appl. Phys. **39**, 4299 (1969).
[2] T. Brauer, S. Gortchakov, D. Loffhagen, S. Pfau, and R. Winkler, J. Phys. D **30**, 3223 (1997).
[3] F. A. V. Ligthart and J. Geboers, Proceedings of the 7th International Symposium on the Science and Technology of Light Sources, Kyoto, The Illuminating Engineering Society of Japan, 1995, p. 267-2688.
[4] C. Roozkranz, F. Ligthart and J. Geboers, Proceedings of the 8th International Symposium on the Science and Technology of Light Sources (Greifswald, Kiebu-Druck GmbH, 1998), pp. 138–139.
[5] Yu. P. Raizer, *Gas Discharge Physics* (Springer, Berlin, 1991).
[6] Atomic Transition Probabilities, a critical data compilation by W. L. Wiese, M. W. Smith, and B. M. Glennon, U.S. Dept. of Commerce, National Bureau of Standards, Washington, DC, 1966.
[7] A. B. Blagoev and T. K. Popov, Phys. Lett. **66A**, 210 (1978).
[8] V. I. Demidov and N. B. Kolokolov, Sov. Phys. Tech. Phys. **23**, 1044 (1978).
[9] J. Weiner, F. Masnouseeuws, and A. Giustisuzor, Adv. At., Mol., Opt. Phys. **26**, 209 (1989).
[10] K. Tachibana, H. Harima, and Y. Urano, Jpn. J. Appl. Phys., Part 1 **21**, 1529 (1982).

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