Excitation of $2p$ levels of argon in Townsend discharges at a high ratio of electric field to gas density

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We have made measurements of the absolute emission intensities, i.e., excitation coefficients of $2p$ levels of argon atom, from $2p_1$ to $2p_9$, by measuring intensities of light originating from $2p$ levels and decaying to $2s$ levels. The excitation coefficients were obtained from the optical signal at the anode of Townsend Ar discharges, after correction for the detector quantum efficiency. Measurements were done for wider ranges of E/N from 50 Td to 9 kTd, than previously reported. Comparisons of our data with other experiments and calculations show different effects of collisional energy transfer for different $2p$ levels at low E/N (pressure above 5 Torr). A comparison of the measured total excitation coefficient for $2p$ levels with the Boltzmann calculations of electron excitation of $2p$ levels from the ground state and via cascading shows the influence of collisional quenching to $1s$ levels at the lower end of the E/N range and strong cascading from higher levels at high E/N.

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I. INTRODUCTION

This paper presents measurements of excitation coefficients for $2p$ excited states of argon, i.e., states from $2p_1$ to $2p_9$ in the Paschen notation, in the wide range of E/N (E is the electric field and N is the gas density) from 50 Td to 9 kTd. The approach used here is to measure absolute intensities of light emitted from the $2p$ level decaying to the $1s$ level in self-sustained argon Townsend discharge. Other experimental measurements of the excitation coefficients for the same transitions were done by Tachibana [1] in the range of E/N between 20 and 500 Td. In his work a non-self-sustained discharge in a drift tube was used to obtain the emission intensities from $2p$ levels.

The electron excitation rate coefficients were calculated from the Boltzmann [1,2] equation by several authors and with different sets of cross sections. Tachibana [1] used momentum transfer cross sections from Hayashi [3], the ionization cross section by Rapp and Englander-Golden [4], and the cross section for excitation of allowed and forbidden ($2p$) states from Egarter [5] and De Heer, Jansen, and van der Kaay [6]. He did not consider cascading from higher levels. Tachibana found good agreement between his experiment and calculations. Using also a two-term Boltzmann code, but a different set of cross sections, Puech and Torchin [2] calculated excitation rate coefficients for $2p$ levels. They used the momentum transfer cross section by Frost and Phelps [7] and for inelastic processes the cross sections calculated by Bretagne *et al.* [8]. They calculated the excitation rates for higher states and gave the upper limits for the cascading contribution to the population of the $2p$ levels. As will be seen later, the results of these two determinations of the excitation coefficients for the $2p$ levels agreed when cascading contributions were taken into consideration.

Determination of the excitation coefficients and cross sections through Boltzmann analyses is complemented by the experimental measurements of the excitation cross sections using electron beam–gas target interactions [9–11]. There are differences between results reported in these works.

Argon plays an important role in the plasma processing of integrated circuits. Optical emissions from the $2p$ to the $1s$ levels of argon have been used for a decade to understand plasma processes in argon or argon-containing mixtures. Using the absolute intensities of those lines in gas discharges to get information on electron behavior, actinometry, etc., can often lead to problems because of a very important role that processes other than direct electron excitation play in populating the $2p$ levels. To what extent should we expect the processes such as cascading, radiation imprisonment, and collisional mixing to affect measured intensities is a key question for anybody who tries to use optical spectroscopy as a diagnostics of argon discharges.

This is our second paper on the measurements of excitation coefficients in argon performed in our drift tube experiment. In our first [12] we presented the measurements for four $2p$ levels ($2p_{1,5,7,9}$) after normalizing the optical signal at the anode to the results of Refs. [1] and [2] at 50 Td. For the work presented here the absolute measurements of nine $2p$ levels have been performed. In Sec. II we explain briefly the experimental setup and the theory of the experiment. The experimental results are presented in Sec. III. Section IV gives a discussion of different factors affecting the measurements and interpretations of data.

II. EXPERIMENT

The experimental apparatus is similar to the one we used for the experiments with nitrogen [13] and hydrogen [14]. The drift tube consists of a pair of plane parallel electrodes, with a diameter of 80 mm and a distance of 17 mm, placed into a close fitting quartz tube. The cathode was made of stainless steel and the anode of graphite so that backscattering of the electrons of anode is minimized.

The self-sustained Townsend discharge between 50 Td and 10 kTd was obtained by running low current discharges at pressures between 30 and 0.14 Torr, respectively. The typical discharge currents were 2–10 μA, for which the operat-

ing voltage was nearly independent of current. A Paschen curve of the argon discharge is shown in Fig. 1 of Ref. [12]. By varying the discharge series resistor between 1 and 5 MΩ, depending on the gas pressure, by minimizing the circuit capacitance, and by often cleaning the quartz tube we were able to run stable, oscillation-free discharges of argon at E/N between 50 Td and 10 kTd.

The light emitted from the discharge was detected using a photomultiplier and a photon counting chain. The selection of lines was done using a monochromator with a spectral resolution of 0.5 nm. The light from the discharge was collected by a lens and projected onto the entrance slit of the monochromator. The spatial resolution of 0.2–0.4 mm was achieved by placing the collimator in front of the monochromator and by moving the entire detector (monochromator and photomultiplier) parallel to the discharge axis by means of the computer driven table.

Determination of the quantum efficiency of the optical system, i.e., the number of detected pulses per each photon emitted at 4π at certain wavelength, was done using a standard tungsten ribbon lamp. The lamp operated at two filament temperatures, 1400 and 1700 K. The elements of the optical system effecting the quantum efficiency were a photomultiplier, monochromator, quartz tube, and vacuum window. For the calibration purposes we used a quartz lens to project, normally 1:1, part of the filament strip onto the entrance slit of the monochromator, passing the light through the quartz tube and window as used in the experiment.

III. EXPERIMENTAL PROCEDURE

The spatial scans of argon lines show an exponential increase of the measured intensity as we scan from the cathode to the anode. In argon we have obtained exponential increases through most of the gap for E/N as high as 5 kTd, but at higher E/N (and below 10 kTd) the exponential increase is limited to a region close to the anode. The maximum values of E/N for which we still had an exponential increase of the signal is much higher than found in some other gases, e.g., nitrogen and hydrogen [13,14]. An exponential increase enables the optical measurements of the ionization coefficient at different E/N. The ionization coefficient gives the average number of electron ionization collisions per unit distance. Equilibrium electron behavior leads to a constant ionization coefficient vs position and therefore to the exponential increase of electron current density. The factors that can be responsible for the loss of exponential growth are predominantly nonequilibrium electron behavior or heavy particle (ion and fast neutrals) excitation.

The procedure for determining the excitation coefficients in our experiment is the following. First the ionization coefficient is obtained from the chosen portion of the exponentially increasing signal. Near the anode the measured signal was deconvoluted into (a) the signal due to the real optical emission, one that can be obtained by using an ideal detector $S_a\exp(-\alpha z)$, where S_a is the optical emission at the anode (to be determined) and α is the ionization coefficient (determined from the curve exponential slope), and (b) rectangularly shaped instrumental spatial resolution function. The procedure of deconvolution gives the anode position and the anode signal S_a.

In Townsend discharges where electron excitation dominates over other processes of level populations and where electrons are in equilibrium with electric field and gas collisions, the electron excitation coefficients of level m are related to the emission signal S_a via

$$\frac{\alpha^m}{N}=\frac{S_a}{j_e}\frac{e}{\frac{\Omega}{4\pi}Q(\lambda)\Delta x N}\frac{A_m}{A_{mn}}, \tag{1}$$

where j_e is the current density at anode, which is equal to the measured current divided by anode area, e is electron charge, Ω is the solid angle subtended by the detector with $\Omega/4\pi$ being 0.0025 s in our experiment, $Q(\lambda)$ is the quantum efficiency of the detector, A_m and A_{mn} are the transition probabilities for the level m and for transition from level m to level n, and Δx is the width of the entrance slit of the monochromator. The electron excitation coefficient given in Eq. (1) represents the average number of electron excitation collisions per unit distance as an electron moves towards the anode. If the rate for the collisional quenching of an excited state is not negligible in comparison with the rate for the spontaneous emission, the correction to the measured S_a can be done by multiplying the right-hand side of Eq. (1) by $(1+N/N_0)$. Here N_0 is the quenching density for the state m (equal to A_m/k_q, where k_q is the rate coefficient for collisional quenching). The data for collisional quenching from $2p$ to $1s$ levels are available in the literature [15–17]. In gas discharges the population of levels occurs also via radiative cascading from higher levels and collisional transfer of energy between energy levels. If those population channels cannot be neglected vs electron excitation from the ground state, then Eq. (1) cannot be used to obtain the electron excitation coefficient. The estimate of the effect of collisions and cascading on the population of $2p$ levels and the estimate of the value of electron excitation can be done through the steady state solutions of the set of coupled time-dependent differential equations for the density of excited $2p$ levels [12,21]. Nevertheless, the results that we present here are obtained after using Eq. (1) to normalize the anode emission signal. We only have to bear in mind that this signal may not be due only to electron excitation from the ground state. The total excitation coefficients for $2p$ levels will be given with and without a correction for the collision quenching of individual $2p$ levels to $1s$ levels [the right-hand side of Eq. (1) multiplied by $1+N/(A_m/k_q^m)$]. The effects of collisional quenching of $2p$ levels resulting in the population of the other $2p$ level (not available in the literature for all $2p$ levels) cancels out in the sum of excitation coefficients for individual $2p$ levels, i.e., in the results for the total excitation coefficients for the $2p$ level.

Based on formula (1) and the performance of the available instrumentation we can make the following estimate of the accuracy of the data. The dominant uncertainty is due to absolute calibration of the emission, which is estimated to be ±10–12%. As mentioned in Sec. II, the calibration of the system was performed by the standard tungsten ribbon lamp. Its temperature has been determined with the aid of a high-precision optical pyrometer calibrated against the primary standard. Other uncertainties include ±3% for the ratio of transition probabilities, 1–3% for the current measurements

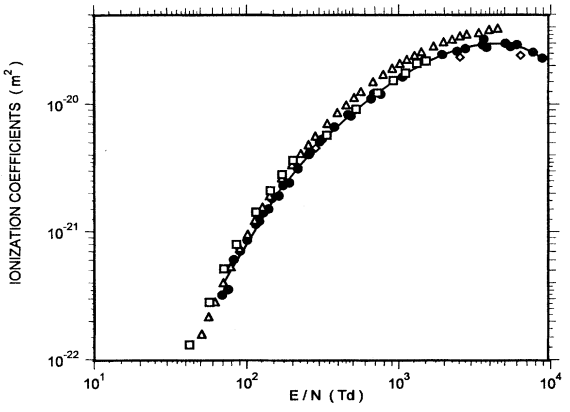

FIG. 1. Ionization coefficients vs E/N. Open symbols are △, Ref. [18]; □, Ref. [19]; ◇, Ref. [20]. Our results are given by solid points. The solid line is the fit through our data.

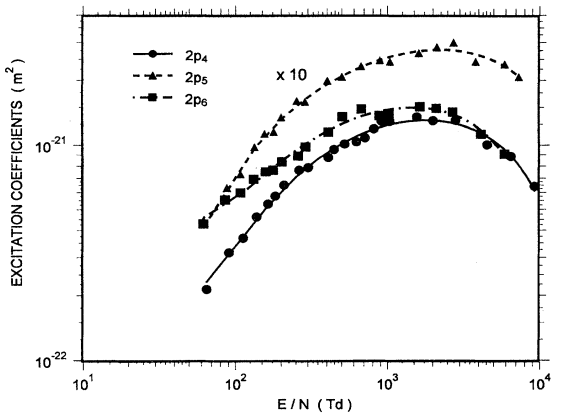

FIG. 3. Excitation coefficients for $2p$ levels: $2p_4$, circles; $2p_5$, triangles ($\times 10$); and $2p_6$, squares.

by the calibrated electrometer, 1–3% for the solid angle determination, 0.5% for the gas number density, and 3–5% for the slit width. The uncertainty of E/N is between 0.5% and 1%. Statistical scatter of the data is of the order 1–3%, depending on the signal level, giving a maximum overall uncertainty of 15% for the experimental data.

IV. RESULTS AND DISCUSSION

In Fig. 1 we show ionization coefficients for Ar vs E/N. Our results, shown by the solid line, are the fit through many data points of ionization coefficients obtained from exponential slopes of spatial scans of emission intensities at different E/N and for different $2p$ transitions. Also included in the figure are the results from Kruithof [18], Lakshminarasimha and Lucas [19], and Phelps and Jelenković [20]. While in Refs. [18] and [19] the ionization coefficients were obtained from discharge current measurements, in Ref. [20] similar optical-type measurements of ionization coefficients were done.

In Figs. 2–4 we have shown the results of our measurements of excitation coefficients of $2p$ levels. Each of the figures 2–4 has the results for three $2p$ levels. We were not able to measure $2p_{10}$ since its transition to $1s$ levels is too far in the infrared to be detected by our system. The curves for different $2p$ levels have a generally similar E/N dependence, with the maxima between 1 and 2 kTd. The exception is $2p_9$ with the maximum at around 800 Td. The excitation coefficients were obtained using Eq. (1) and measured emission intensities at the anode S_a and were without correction for collision quenching. Analyses of the effect of the $2p$ level population due to collisional mixing within $2p$ levels and collisional quenching to $1s$ levels, and cascading from higher s and d levels show that their effect can be significant at specific pressures and E/N values [12,21]. At pressures above 1 Torr collisional population mixing makes the strong contribution to the population of some $2p$ levels [21]. Levels $2p_2$–$2p_5$ that energetically lie close to each other have higher collision mixing, exceeding by far quenching to $1s$ levels. The $2p_1$ has the lowest total collisional quenching.

In Table I we compare the excitation coefficients for $2p$ levels obtained in our experiment to those from Refs. [1] and [2], for E/N of 100 Td. There are two values in the column

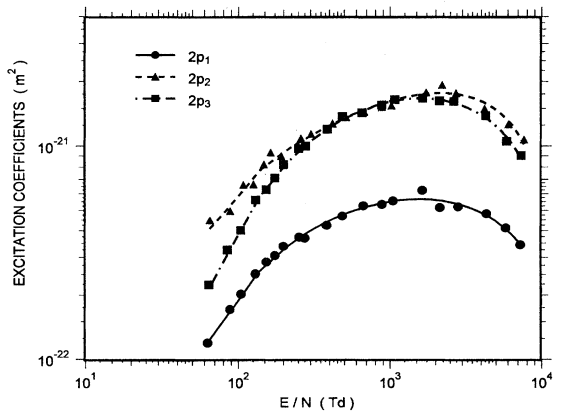

FIG. 2. Excitation coefficients for $2p$ levels: $2p_1$, circles; $2p_2$, triangles; and $2p_3$, squares.

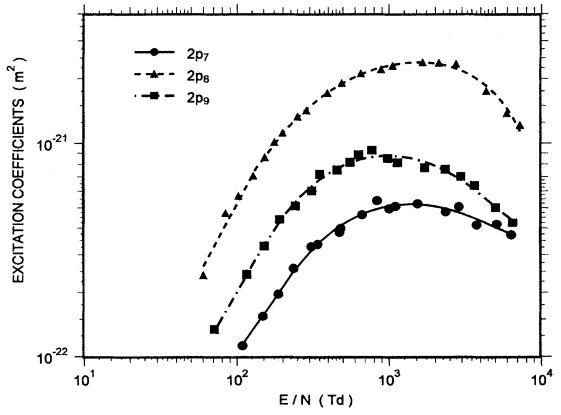

FIG. 4. Excitation coefficients for $2p$ levels: $2p_7$, circles; $2p_8$, triangles; and $2p_9$, squares.

TABLE I. Emission excitation coefficients at 100 Td in units of 10^{-22} m^2. The number is parentheses gives excitation of the level due to cascading.

Level	Ref. [1]	Ref. [2]	This work
$2p_1$	2.8	1.7 (0.01)	1.8
$2p_2$	1.27	0.48 (0.4)	5.7
$2p_3$	2.75	0.7 (0.8)	3.8
$2p_4$	2.45		3.4
$2p_5$	1.49	2.15 (1.1)	0.7
$2p_6$	3.2	0.86 (0.72)	5.5
$2p_7$	1.04	1.14 (1.1)	1.0
$2p_8$	2.9	1.0 (1.22)	5.1
$2p_9$	3.3	1.22 (3)	1.8
$2p_{10}$	3.5	0.8 (6.0)	
$2p$	24	11.3 (16.1)	28.8

for data from Ref. [2]: first is the calculated direct electronic excitation and second (in parentheses) is due to cascading from upper levels. The total excitation coefficients from Ref. [2] are therefore the sum of two values. Reference [2] gives only the sum of excitation coefficients for $2p_4$ and $2p_5$.

From a comparison of the data given in Table I one can see that only for $2p_1$, the level expected to be the least affected by collisions and cascading, are our results in good agreement with the calculated value. For other $2p$ levels both experimental results given in Table I, i.e., from Ref. [1] and this work, are either higher or lower than given by theory [2]. In those cases Tachibana's results are closer to the results by Puech and Torchin than our results. This observation makes sense since Tachibana's experiment ran at lower pressures than ours, lowering the effects of collisions on the populations of the levels. A comparison of experiments and theory (see Table I) suggests that the population mixing between $2p$ levels increases the population of $2p_2$ and $2p_3$ from what it would be in the case of pure electron excitation. The same collisional mixing as well as collisional quenching to $1s$ levels apparently transfer population away from $2p_7$ and $2p_9$.

Puech and Torchin [2] have found that cascading from upper levels, notably $2s$ and $3d$, can have a larger contribution to the population of $2p$ levels than the direct electron excitation. Results from Ref. [2] given in Table I for electron excitation and cascading (numbers in parentheses) show that even at low E/N cascading is significant for most of the $2p$ levels. Here again one can see that $2p_1$ is the least affected. The work of Ref. [2] did not take into account imprisonment of radiation from optically allowed higher-lying levels. Higher pressures can enhance cascading through the imprisonment of radiation from s and d levels, which can also decay to $2p$ levels [22].

As already pointed out, one of the results shown in Table I is the good agreement for $2p_1$ between experimental and calculated values of excitation coefficients. Estimation of contributions to level populations due to collisional quenching to $1s$ levels, collisional mixing, and cascading, including the effect of imprisonment of radiation revealed that $2p_1$ is basically free of contributions from other excitation channels besides direct excitation. Support of this statement are measurements of decay rates of the $2p$-$1s$ transition upon excitation of Ar by a short electron pulse by Cooper *et al.* [23], who have shown that only the $2p_1$-$1s_2$ transition has a decay time close to the measured radiative lifetime.

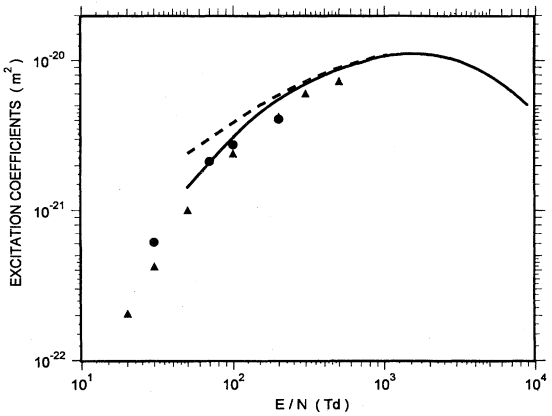

FIG. 5. Excitation coefficients for $2p$ levels of argon. Solid triangles are experimental data by Tachibana [1] and solid circles are calculations by Puech and Torchin [2]. Our results are shown by the solid line. The dashed line presents our data for total excitation coefficients after correcting the excitation coefficients for individual $2p$ levels for the collisional quenching to $1s$ levels.

The $2p_9$ level has an emission excitation cross section that peaks at lower electron energies (22 eV) and falls off more rapidly at higher energies, as compared to the cross sections of the other $2p$ levels [10]. By comparing Figs. 2–4 one can see that the maximum of the excitation coefficient for $2p_9$ lies at lower E/N than for other $2p$ levels. This can be due to the different shape of the cross sections, but in the absence of intensive cascading contribution. This work appears to support suggestions [20,24] that excitations via cascading from forbidden transitions (such as $3d'_4$ cascading to $2p_9$) are less important at higher E/N values than the excitation through allowed transitions that cannot populate $2p_9$ but can populate other $2p$ levels. In the later excitation kinetics scheme [2], $2p_9$ can be populated from higher levels if the collisional mixing of $3d$ and $2s$ levels to some forbidden levels takes place.

Figure 5 shows a comparison of the total excitation coefficients for the $2p$ levels obtained in this work with results given by Tachibana [1] and Puech and Torchin [2]. Our data, given by the solid line, were obtained after summing the excitation coefficients for individual levels ($2p_1$–$2p_9$) at different E/N. They have the same E/N dependence as Tachibana's results (given by open triangles), but are higher by about 15%. Collisional mixing between $2p$ levels cancels out in the total excitation coefficient. A similar E/N dependence for two data sets and the fact that our results are higher can be explained with the radiation trapping of optically allowed transitions since imprisonment is nearly independent of pressure for pressures above about 1 Torr. The importance of the collisions for the decay of the $2p$ level to the $1s$ level can be seen from the dashed line obtained after correction of the excitation coefficients for the collisional quenching, i.e., applying a modified Eq. (1) (see the discussion in Sec. III).

When compared with calculated values for excitation that

includes electron and cascading excitation [2], our results are in good agreement with Ref. [2] below 100 Td and have a different E/N dependence at higher E/N. According to Fig. 5, there is a discrepancy between experiments and theory that assumes cascading contribution mainly from forbidden levels at high E/N.

V. CONCLUSION

We have measured absolute intensities or excitation coefficients for nine $2p$ levels of argon, from $2p_1$ to $2p_9$. The excitation coefficients have a similar E/N dependence with the broad maxima around 1.5 kTd. The exception is the $2p_9$ level, whose maximum is at 800 Td.

Our results at the lower end of E/N (below 500 Td) were compared with the data obtained by Tachibana, who used non-self-sustained Ar discharge at lower pressure than ours. A comparison between two experimental sets of data shows that our results can be much higher for some and lower for other $2p$ levels than Tachibana's. We can interpret this as a difference in the pressure effects on different excited levels. A comparison between the two experimental sets of data, from Ref. [1] and this work, with the calculated results (two-term Boltzmann calculations) by Puech and Torchin [2] shows that there are some $2p$ levels with significant collision population ($2p_2$ and $2p_8$). This is different from the behavior of the $2p_5$ and $2p_9$ levels, which are apparently efficiently quenched to either $1s$ levels (most likely dominating for low-lying $2p_9$) or other $2p$ levels (quenching from $2p_5$ is almost entirely to the nearby $2p$ levels) [18]. The effect of high density we had in our experiment for E/N between 50 Td and 1 kTd (30 and 0.5 Torr, respectively) on the increased level population is twofold: population of levels via collisional mixing and enhanced cascading from resonant levels due to radiation imprisonment. Thorough analyses of those effects on the population of levels at the pressures of our experiments are currently under way in our laboratory.

We can interpret agreement between calculated [2] and measured values for the excitation coefficients for $2p_1$ as the consequence of a small contribution of quenching and cascading vs electron excitation, as suggested in Ref. [2]. But experiments are not supporting high excitation coefficients of $2p_9$ due to the combined electron and cascading excitations, as given by Puech and Torchin. The fact that the maximum of this level is at the lowest E/N (below 1 kTd) can be viewed as another argument of low cascading effects onto $2p_9$. This level is the only level that can be populated from optically forbidden levels. Experiments suggest a small population of these levels at high E/N. In light of our results and discussions we recommend using the 750.4-nm line ($2p_1$-$1s_2$ transition), normally very strong under most discharge conditions, for optical diagnostics of argon discharges.

The total excitation coefficients for $2p$ levels given by Tachibana are lower than our results, but the two sets of data have similar E/N dependences. The difference (about 15%) is within the estimated total experimental errors. The agreement between our results and those calculated by Puech and Torchin is good at low E/N (below 100 Td), while at higher E/N the discrepancy arises due to different E/N dependences of excitation coefficients.

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