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Measurement of the electron density in atmospheric-pressure low-temperature argon discharges by line-ratio method of optical emission spectroscopy

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Abstract

A new collisional–radiative model for atmospheric-pressure low-temperature argon discharges is proposed, which illustrates the significant effect of electron density on the excited atom population distribution. This makes it possible to determine the electron density from the intensity ratio of emission lines of excited atoms. Results of this new method in several types of atmospheric-pressure discharges are found to be in agreement with those of the Stark broadening method and the electric model over a wide electron density range 10¹¹–10¹⁶ cm⁻³.

(Some figures in this article are in colour only in the electronic version)

The electron density is one of the most fundamental parameters in gas discharges and plays a very important role in understanding the discharge physics and optimization of the operation of plasmas [1, 2]. Typical methods to measure the electron density include the use of a Langmuir probe [3], microwave interferometry [4], laser Thomson scattering (LTS) [5] and optical emission spectroscopy (OES) [6]. However, in atmospheric-pressure low-temperature discharges, both the probe and the microwave-based methods are difficult to use due to the small plasma dimensions and strong collisional processes. LTS has been proved to be effective but challenging because of the low signal and excessive stray light, as well as the complicated experimental setup [7]. However, the OES-based technique has the advantages of being non-intrusive, inexpensive and convenient. There are three major OES techniques to determine the electron density in low-temperature plasmas. One OES method involves the investigation of the Stark broadening of emission line profiles, such as that of hydrogen Balmer lines [8]. At electron densities lower than ~10¹³ cm⁻³ and at atmospheric pressure, this method is inappropriate since the van der Waals broadening or Doppler broadening becomes the dominant broadening process. Another method is to analyse the continuum radiation if it is observed, such as in some recombining plasmas [9]. The last one is the line-ratio method, in which the intensity ratio of emission lines is related to the electron density by a collisional–radiative model (CRM) [10]. This method has been successfully used in low- and medium-pressure discharges [10–12]. In this work, with a CRM of atmospheric-pressure discharges, a line-ratio method to determine the electron density from the mostly observed optical emission of argon 2p–1s transitions (in Paschen’s notation) is introduced.

To obtain the relationship between the electron density and the line-ratios of optical emissions, the effect of electron density on the excited atom kinetics should be analysed. In
In regime (c) (high electron density \( \sim 10^{15} - 10^{16} \text{ cm}^{-3} \)), the electron-impact transfer dominates the atom-collision transfer. Similar kinetic pictures of the 2p multiplet have also been obtained in previous argon CRMs [13–15].

The variation of dominant processes of the 2p multiplet, being caused by the variation of electron density, can significantly affect the atomic population distribution, as shown in figure 2. In figure 2(a) of the kinetic regime (a), the population of 2p, 2p, and 2p levels is larger than nearby levels, because these three levels have smaller rate coefficients of atom-collision transfer and thus have a smaller depopulation rate [16–18]. In regime (b), excitation from 1s levels becomes the dominant production process. Since the excitation rate coefficients from 1s levels to 2p, 2p, and 2p levels are much smaller than those to the other 2p levels [19], one can observe very small populations of 2p, 2p, and 2p levels in figure 2(b). In regime (c), strong electron-impact transfer processes between excited levels makes a Boltzmann-like distribution, with the population of each level nearly in proportion to its degeneracy degree, as shown in figure 2(c). Note that the detailed population distribution of 2p levels such as those in figure 2 cannot be obtained from the previous CRMs due to the use of some improper simplifications. Firstly, an effective level was used instead of the individual levels with close excitation energies. For example, 2p, 2p, and 2p were combined into one effective level. Thus the difference in populations among these levels, as seen in figure 2, was not shown in the previous CRMs. Besides, an empirical formula was adopted for collisional transfer processes in previous works, in which the large difference in rate coefficients for different 2p levels was neglected. Therefore, the important characteristic of large 2p, 2p, and 2p population in regimes (a) and (b) will not be found in those models. In order to obtain the relationship between the electron density and the population distribution (thus line-ratios), we use individual 2p levels and experimental state-to-state rate coefficients in the new CRM [16–19].

The excited atom population distribution is generally affected by the electron density \( n_e \), the electron temperature \( T_e \) and the gas temperature \( T_g \). However, for the atmospheric-pressure low-temperature argon discharges used in this work, the electron temperature (or effective electron temperature) is found to be in a narrow range 1–2 eV and the gas temperature is in the range 300–600 K [20–23]. Therefore, their effect on the distribution is very small compared with the electron density, whose range of variation can be several orders of magnitude greater. Therefore, the kinetic picture under typical conditions shown in figures 1 and 2 can be used. The next important parameter is the plasma dimension. Even though its value may vary over a wide range (0.1–10 mm), it has a quite limited effect on the population distribution compared with the electron density, since the diffusive processes are strongly limited by the collisions at atmospheric pressure.

Atmospheric-pressure plasmas are optically thin for photons of non-resonance lines due to large collisional broadening [24, 25]. Therefore, the line-ratio of these optical emissions is

\[
\frac{I_1}{I_2} = \frac{A_1 n_1}{A_2 n_2}.
\]

\( I_1 \) and \( I_2 \) are the observed intensities of the lines, while \( A_1 \) and \( A_2 \) are the Einstein coefficients of the transitions. This expression can be found in those models. In order to obtain the relationship between the electron density and the population distribution (thus line-ratios), we use individual 2p levels and experimental state-to-state rate coefficients in the new CRM [16–19].
under the discharge condition in figure with the measured line-ratio the range 10
transfer. Even though one can use other sets of 2p levels while they have similar rate coefficients for electron-impact has a smaller rate coefficient of atom-collision transfer than 2p

Here \( l_1 \) and \( l_2 \) are the intensities of emission lines in 2p–1s transitions, \( A_1 \) and \( A_2 \) are the Einstein coefficients and \( n_1 \) and \( n_2 \) are the densities of two different 2p levels. One can obtain the electron density by comparing the population ratio \( n_1/n_2 \) in the distribution given by the CRM (as in figure 2) with the measured line-ratio \( I_1/I_2 \). As seen in figure 2, there are three groups of 2p levels with different relationships to the variation of electron density. For our purpose, we can select a representative 2p level from each group, for example, 2p\(_1\), 2p\(_3\) and 2p\(_6\) levels. The population ratios \( R_{13} (n_{2p1}/n_{2p3}) \) and \( R_{36} (n_{2p3}/n_{2p6}) \) are plotted as functions of electron density in figure 3, under the condition shown in figure 1. It is found that \( R_{13} \) decreases significantly with the electron density in the range \( 10^{11}–10^{13} \) cm\(^{-3}\), during the transition from regime (a) to regime (b). This is because 2p\(_1\) and 2p\(_3\) levels have similar rate coefficients of excitation from the ground state, but very different excitation rate coefficients from the 1s levels. Similarly, \( R_{36} \) increases significantly with the electron density during the transition from regime (b) to regime (c), since 2p\(_6\) has a smaller rate coefficient of atom-collision transfer than 2p\(_3\) while they have similar rate coefficients for electron-impact transfer. Even though one can use other sets of 2p levels to determine the electron density as well, this set (2p\(_1\), 2p\(_3\) and 2p\(_6\)) has an additional advantage that the emissions from these levels are spread over a very narrow wavelength range (2p\(_1\)–1s\(_2\), 750.4 nm; 2p\(_3\)–1s\(_4\), 738.4 nm; 2p\(_6\)–1s\(_3\), 763.5 nm). This makes the OES measurement, as well as the intensity calibration, relatively easy.

By using the population ratios \( R_{13} \) and \( R_{36} \), the electron densities in three types of atmospheric-pressure discharges are measured, including an rf glow discharge, an rf filament discharge and a microwave microdischarge [22, 23]. The operating parameters and plasma parameters of those discharges are listed in table 1. From figure 4, it is found that the results of the line-ratio method are in good agreement with those of the Stark broadening method [22, 23] and the electric model [22, 26]. The limited difference between results of OES measurement and the electric model can be caused by the non-uniformity of discharges, since the former gives an averaged result from the emission intensity while the latter assumes a uniform plasma. The error bar in figure 4 is caused mainly by the uncertainty of the experimental rate coefficients of atom-collision population transfer [16–18].

This line-ratio method can also be used for the atmospheric-pressure non-equilibrium discharges with relatively high gas temperature, say, \( T_e \approx 1000–2000 \) K [21]. According to the ideal gas law, the gas density \( n_g \) will decrease when \( T_e \) increases. As a result, in figure 1, both the reaction rate of electron-impact excitation from the ground state (gsexc) and that of atom-collision population transfer (atom-trans) become smaller. The transition between regimes (a) and (b) or that between (b) and (c) occurs at lower electron densities. As a result, the \( R_{13} \) and \( R_{36} \) curves in figure 3 will move leftwards.

The effect of \( T_e \) on the line-ratio of two excited levels can be generally estimated as \( f \approx \exp (\Delta E/T_e) \) where \( \Delta E \) is the energy gap between two levels [10]. For argon 2p levels used here, \( \Delta E \approx 0.2 \) eV \( \ll T_e \) and thus \( f \approx 1 \). In fact, the \( T_e \) effect on these line-ratios is not important unless \( T_e \) is as low as 0.1–0.2 eV, such as in some recombing plasmas [9].

In this method, one utilizes the significant variation of the line-ratio, being nearly proportional to the logarithm of the electron density (see figure 3), during the variation of dominant kinetic processes. Due to this nonlinear dependence of line-ratio on the electron density, the uncertainty from either the OES measurement or the CRM calculation will be enlarged.
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a wide electron density range. This method may have
three types of typical atmospheric-pressure discharges over
spectroscopy. The validity of this method is confirmed in
collisional–radiative model with those from optical emission
the line-ratios of argon 2p–1s transitions predicted from a
discharges. The electron density is obtained by comparing
electron density is proposed for atmospheric-pressure argon
atmospheric pressure \[ gas \text{ discharges, such as helium, neon, nitrogen and air, at }
heavy particles, are also important in many other types of
including the electron-impact processes and collisions between
gases when the proper CRMs are developed in the future.

Figure 4. Comparison of electron density from the line-ratio
method, the Stark broadening method and the electric model in three
types of atmospheric-pressure argon discharges.

Therefore, the line-ratio method may not provide the electron
density measurement as accurately as the LTS. However, due
to the nonlinear dependence, the line-ratio method does not
suffer from the low signal-to-noise ratio problem as the LTS
at low electron densities. This is a unique advantage of all the
line-ratio methods for low-, medium-, high- and atmospheric-
pressure discharges [10–12].

The kinetic processes involved in argon discharges,
including the electron-impact processes and collisions between
heavy particles, are also important in many other types of
gas discharges, such as helium, neon, nitrogen and air, at
atmospheric pressure [24,27]. Similar line-ratio methods,
using the variation of dominant mechanisms of excited
particles versus the electron density, can be expected in those
gases when the proper CRMs are developed in the future.

In conclusion, a new line-ratio method to measure the electron
density is proposed for atmospheric-pressure argon
discharges. The electron density is obtained by comparing
the line-ratios of argon 2p–1s transitions predicted from a
collisional–radiative model with those from optical emission
spectroscopy. The validity of this method is confirmed in
three types of typical atmospheric-pressure discharges over
a wide electron density range. This method may have
potential applications in the recently developed spatially
and temporally resolved optical diagnostics for atmospheric-
pressure discharges [28,29].

### Table 1. Operating parameters and plasma parameters for three types of argon discharges.

<table>
<thead>
<tr>
<th>Source</th>
<th>Rf glow discharge</th>
<th>Rf filament discharge</th>
<th>Microwave microdischarge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>760 Torr</td>
<td>760 Torr</td>
<td>900 MHz, continuous</td>
</tr>
<tr>
<td>Power</td>
<td>~100 W</td>
<td>~100 W</td>
<td>~740 Torr</td>
</tr>
<tr>
<td>Plasma dimensions</td>
<td>~100 × 100 × 5 mm</td>
<td>~5 × 0.1 × 0.1 mm</td>
<td>~1 × 0.1 × 0.1 mm</td>
</tr>
<tr>
<td>Electron density</td>
<td>(10^{11}–10^{12} \text{ cm}^{-3})</td>
<td>(10^{15} \text{ cm}^{-3})</td>
<td>(10^{13}–10^{14} \text{ cm}^{-3})</td>
</tr>
<tr>
<td>Electron temperature</td>
<td>~1–2 eV</td>
<td>~1–2 eV</td>
<td>~1–2 eV</td>
</tr>
<tr>
<td>Gas temperature</td>
<td>~300–600 K</td>
<td>~300–600 K</td>
<td>~300–600 K</td>
</tr>
</tbody>
</table>

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