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A comparison among optical emission spectroscopic methods of determining electron temperature in low pressure argon plasmas

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In this article, four kinds of optical emission spectroscopic methods of determining electron temperature are used to investigate the relationship between electron temperature and pressure in the cylindrical plasmas of dc glow discharges at low pressures in laboratory by measuring the relative intensities of ArI lines at various pressures. These methods are developed respectively on the basis of the Fermi–Dirac model, corona model, and two kinds of electron collision cross section models according to the kinetic analysis. Their theoretical bases and the conditions to which they are applicable are reviewed, and their calculation results and fitting errors are compared with each other. The investigation has indicated that the electron temperatures obtained by the four methods become consistent with each other when the pressure increases in the low pressure argon plasmas.

Keywords: plasma diagnostics, gas discharge, optic emission spectroscopy, electron temperature
PACC: 5270, 5280, 5225P, 5225L

1. Introduction

Low pressure dc glow discharge, an important mode in gas discharges, is one of the most common modes for laboratory plasmas.[1] The research of this sort of discharge can be used as a reference to the study of other types of plasmas. Generally, the positive column (PC) region of a low pressure glow discharge occupies a majority of a chamber. Owing to the relatively low gas temperature in this region and the current formed by electronic-impact ionization, the dc glow discharge can generate weakly ionized non-equilibrium plasmas, of which spectral lines are mostly caused by spontaneous atomic radiation.

In the above situation, it is inappropriate to use the conventional Boltzmann plot method, which is based on a traditional local thermodynamic equilibrium (LTE),[2−5] to calculate the electron temperature (T_e) because the population density of excited states does not follow the Boltzmann law. Therefore, it is necessary to seek for new models or methods to calculate T_e on the basis of analysing the atomic radiation mechanism.

In this article, electron temperatures, with pressure increasing, are calculated using the following four models: Fermi–Dirac model, corona model, and two kinds of electron collisional cross section model based on kinetic analysis. The experimental data for calculation are obtained by measuring relative intensities of ArI lines at various pressures. Furthermore, the spectroscopic results are compared with those measured by a single probe to validate the reliability of the former. Moreover, the relationship among those methods and the conditions to which they are applicable are investigated.

2. Experiment scheme

Figure 1 shows the schematic diagram of our experimental setup and diagnostic methods. The experiment is carried out in a vacuum chamber of glass cylinder with a 20 cm diameter, which is divided into three sectors: sectors on both ends are of stainless steel and the intermediate one is of transparent glass. The background pressure of the vacuum chamber is 10^{-2} Pa. Argon gas is introduced into the chamber through an adjustable flowmeter. Glow plasmas are generated by a high dc voltage applied across the circular electrodes on both ends of the chamber. The radii of the circular electrodes both are 4.0 cm and the distance between them is 38 cm. The pressure of working gases and electric power can be adjusted according to experimental requirements.

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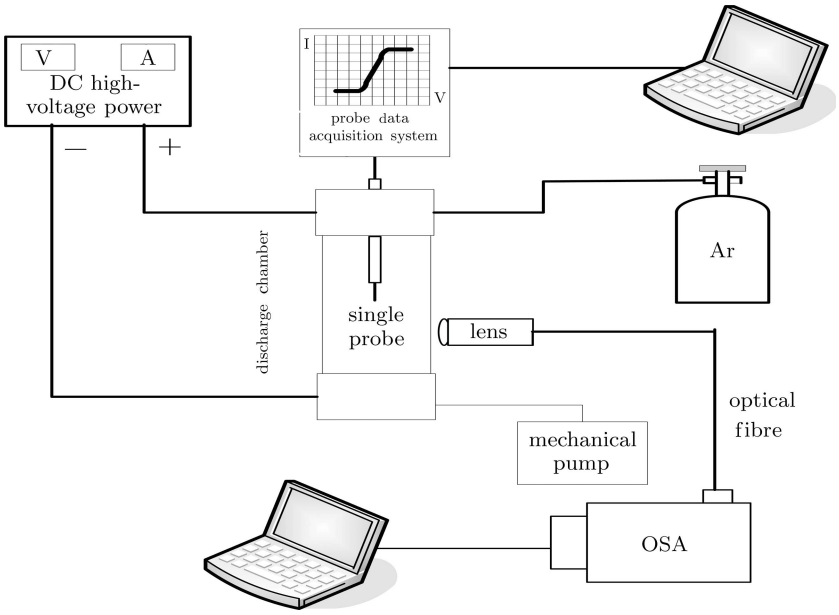


Fig.1. Experimental setup and diagnostic methods.

A grating spectrometer (model WGD-8) manufactured by Tianjin Gangdong Corporation with a 0.5 m focal length, a resolution of 0.05 nm, an entrance slit of 50 μm and a grating of 1200 grooves mm^{-1}, is used to measure the intensities of spectral lines. A photomultiplier tube (PMT), whose response ranges from 200 to 800 nm, is used to collect photons, and its output signal is transmitted through AD card to a computer after being amplified. In order to calibrate the whole optic system including optical fibre, a tungsten ribbon lamp is employed. The calibration results are used to modify the intensities of spectral lines for the relevant calculation.

A single probe is located on the axis of cylindrical glow discharge region. The probe signal is received by integrated data acquisition system with our designed USB2.0 interface. The sampling rate of each channel is at 1 MHz and data processing codes are programmed with Matlab.

3. Experimental data

Ordinarily, in order to acquire an electron average energy in plasmas by using an optic emission spectroscopy (OES) method, the kinetic process contributing to the population and depopulation between excited levels and ground levels should be known. In low pressure glow plasmas, the conventional Boltzmann plot method based on the LTE theory is inaccurate in determining T_e because of the deviation of atom or ion densities in excited levels from Boltzmann distribution.[2] Thereupon, in this article four kinds of physical models are introduced to calculate T_e in DC glow plasmas on the basis of analysing the mechanism of the population and depopulation in the atom excited levels.

3.1. Fermi–Dirac model

In spectroscopic methods of determining T_e, it is generally assumed that a steady state exists in the plasma and gives rise to a Boltzmann distribution for excited-state populations as a function of the upper-level population. The assumption actually avoids the details of population and depopulation process. However, in the experiment, a phenomenon has been found that the natural logarithm of excited-state population calculated by OES-measured intensities of spectral lines in a low pressure glow plasma is not a linear function of the upper-level population. That is, the tendency of plots in Boltzmann figures can deviate from a straight line. In order to solve the problem, the Fermi–Dirac distribution function in quantum statistics has been introduced by Fannin *et al.*[6] As the trend of the above function is identical with experimental points, the model is chosen to compute T_e in our calculation. The Fermi–Dirac model can be expressed as

$$\ln\left[\frac{I_{ij}\lambda_{ij}}{g_i A_{ij}}\right] = \ln[\exp(\varepsilon_i - \mu)/kT + 1]^{-1} + C, \quad (1)$$

where I_{ij} and λ_{ij} are intensity and wavelength of spectral lines respectively, which can be read out from the

spectrometer directly, constant C is the scaling coefficient between relative population and theoretical population. A_{ij}, g_i, ε_i and μ are the Einstein coefficient, Lande factor, energy of the upper level and chemical potential, respectively. The corresponding parameters in our calculation are obtained from NIST.[7]

A simplified formula for fitting is as follows:

$$y = -\ln(\exp((x-2.2)/T_{\mathrm{e}})+1) + \mathrm{const}, \qquad (2)$$

where the chemical potential is 2.2 eV, T_{e} is in units of eV. A multiple Levenberg–Marquardt iterative method is used for the nonlinear least square fitting. A curve which approaches the Fermi–Dirac distribution can be acquired after several iterations. The electron temperatures obtained by using the above method under seven different pressures are listed in Table 1. In Fig.2 the fitting curve under 30 Pa is presented.

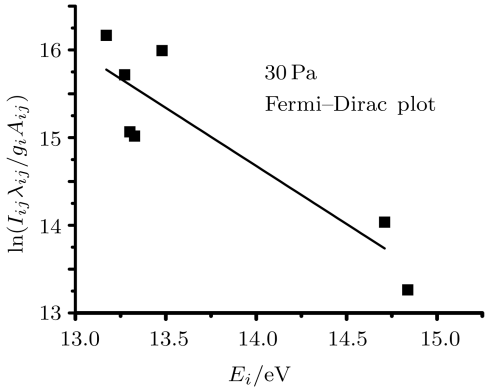


Fig.2. Fitting curve using Fermi–Dirac model under 30 Pa.

Table 1. T_{e} calculated by Fermi–Dirac model under seven discharge pressures, R is the correlation coefficient, and Chi^2 is the sum of the squares of the deviations of the theoretical curve(s) from the experimental points for a range of independent variables, divided by the number of degrees of freedom.

pressure/Pa	Fermi–Dirac plot		
	T_{e}/eV	R^2	Chi^2
10	2.784 ± 3.327	0.135	0.336
15	1.762 ± 1.004	0.433	0.302
20	1.541 ± 0.704	0.546	0.252
22	1.329 ± 0.590	0.561	0.318
25	1.149 ± 0.400	0.676	0.261
28	0.890 ± 0.244	0.728	0.294
30	0.755 ± 0.167	0.805	0.264

It can be seen from Table 1 that the statistical errors at low pressures are relatively large because of weak intensities of spectral lines emitted from low density laboratory plasmas. Furthermore, the descending tendency of T_{e} with increasing pressure can be found obviously.

3.2. Corona model

Owing to the typical electron density ranging from 10^9 to $10^{11}\,\mathrm{cm}^{-3}$ for low pressure dc glow plasmas in our laboratory, the direct excitation from the ground state with radiative decay will dominate over the production and destruction of excited energy levels. This indicates that corona balance is a primary process in low pressure and density plasmas, according to Fujimoto's results.[8]

Gordillo-Vazquez *et al*[9] have investigated the corona model and obtained a modified Boltzmann formula as follows:

$$\ln \frac{I_{ij}\lambda_{ij}\sum\limits_{i>j} A_{ij}}{A_{ij}a_{1i}} = -\frac{E_{1i}}{kT_{\mathrm{e}}} + \mathrm{const}, \qquad (3)$$

where I_{ij} and λ_{ij} are, respectively, the intensity and wavelength of spectral lines which could be read out from spectrometer directly, A_{ij} is the Einstein coefficient, E_{1i} is the excitation energy of level i, a_{1i} is the coefficient in an exponential approximation of electron impact excitation rate coefficient from ground state 1 to level i. Table 2 is a parameter table for fitting T_{e} using Eq.(3). Figure 3 is the line fitted by Eq.(3) under 30Pa.

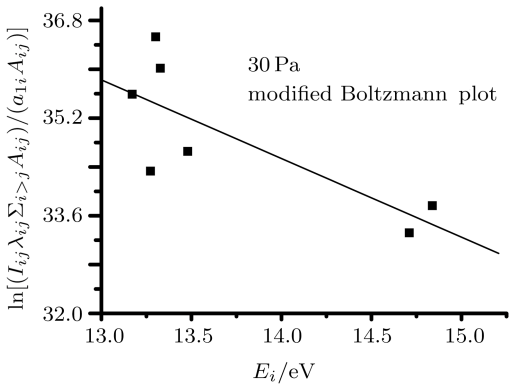


Fig.3. Fitting line using corona model under 30 Pa.

Table 2. Parameters for fitting T_e obtained using corona model.

λ_{ij}/ nm	E_i / eV	$A_{ij}/10^8 s^{-1}$	f_{1i}	g_i	p_i	a_{1i}	$\sum_{i>j} A_{ij}/10^8 s^{-1}$	Number of radiative transitions
687.1	14.71	2.78×10^{-2}	1.97×10^{-2}	3	3.62	4.598×10^{-10}	0.0364	3
696.5	13.33	6.39×10^{-2}	2.79×10^{-2}	3	2.37	8.017×10^{-10}	0.3522	5
703.0	14.84	2.67×10^{-2}	1.41×10^{-2}	5	3.87	3.230×10^{-10}	0.0518	5
706.7	13.30	3.80×10^{-2}	2.85×10^{-2}	5	2.36	8.229×10^{-10}	0.3457	4
720.7	15.02	2.48×10^{-2}	1.16×10^{-2}	3	4.32	2.590×10^{-10}	0.04325	5
750.3	13.48	4.45×10^{-1}	1.25×10^{-1}	1	2.45	3.508×10^{-9}	0.4474	3
751.4	13.27	4.02×10^{-1}	1.14×10^{-1}	1	2.34	3.307×10^{-9}	0.4020	2
763.5	13.17	2.45×10^{-1}	2.14×10^{-1}	5	2.30	6.308×10^{-9}	0.3443	4

Table 3. T_e and x results obtained using corona model, σ is the standard deviation of the fit.

pressure/Pa	T_e/eV	$R^2_{T_e}$	σ_{T_e}	x	R^2_x	σ_x
10	1.272 ± 1.430	0.17	1.15	1.07	0.11	0.59
15	1.324 ± 0.828	0.39	0.80	1.66	0.42	0.48
20	1.194 ± 0.661	0.45	0.79	2.08	0.55	0.50
22	1.063 ± 0.454	0.58	0.68	2.42	0.57	0.56
25	0.944 ± 0.406	0.57	0.77	2.78	0.68	0.51
28	0.920 ± 0.388	0.53	0.81	3.61	0.74	0.53
30	0.776 ± 0.280	0.61	0.82	4.26	0.81	0.50

It can be seen from Table 3 that the tendency of T_e with pressures varying, calculated by the corona model, is the same as that obtained by the Fermi–Dirac model. In order to verify the validation of using corona model in our plasma, an effective principal quantum number p_i for an excited state is introduced. For optically thin plasmas, the relative population density of energy level i of argon follows the expression

$$\frac{N_i(p_i)}{g_i(p_i)} \propto p_i^{-x}, \tag{4}$$

where $p_i = \sqrt{\frac{E_H}{E_\infty - E_i}}$, E_H is the Rydberg constant (13.6eV), E_∞ is the ionization energy of working gas, and E_i is the excitation energy of level i. By taking the natural logarithm of Eq.(4), Eq.(5) can be obtained as

$$\ln \frac{I_{ij}\lambda_{ij}}{A_{ij}g_i} = -x \ln p_i + \text{const.} \tag{5}$$

Figure 4 shows the relative population density of Ar energy level i as a function of its effective principal quantum number p_i under 30 Pa. The values of x in the above expression under various pressures are listed in Table 3. With increasing pressure, x values increase from 1.07 to 4.26. Plasma density correspondingly grows from 10^9 to 10^{11}cm^{-3} according to Fujimoto's results.[8] Moreover, the densities of our plasmas, which are measured by a single probe and listed in Table 4, are just in the range. Therefore, it can be verified that our non-equilibrium plasma satisfies corona balance condition.

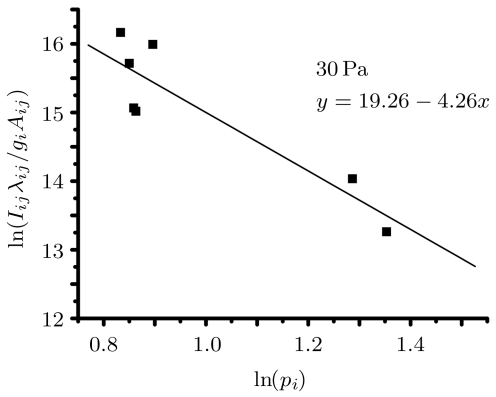


Fig.4. Relative population density of Ar energy level i as a function of p_i under 30Pa.

Table 4. T_e and N_e measured by a single probe.

pressure/Pa	T_e/eV	$N_e/10^{11}$cm^{-3}
10	3.34	0.68
15	3.24	0.83
20	3.19	0.91
23	3.75	1.00
25	3.40	1.03
27	3.10	1.14
30	3.07	1.17

3.3. Two kinds of electron excited cross section models

Assume that the population of upper level i is predominant due to direct electron impact excitation in a low pressure discharge plasma, then we will have

$$N_i = N\int_{E_i}^{\infty} f_{\rm e}(E)\sigma_{\rm e}(E){\rm d}E, \tag{6}$$

where N is the number of gas particles, E is the electron energy, E_i is the excitation energy of level i, $f_{\rm e}(E)$ is the electron energy distribution function (EEDF) which can be considered as the Maxwellian distribution in the PC region of our dc glow plasmas. Ling[10] has suggested two kinds of simplified cross sections for the integral of Eq.(6), and they are

$$\sigma_{\rm e}(E) = \begin{cases} 0 & (E < E_i), \\ \sigma_{\rm e\ max} & (E \geq E_i), \end{cases} \tag{7a}$$

$$\sigma_{\rm e}(E) = \begin{cases} 0 & (E < E_i), \\ \left(\dfrac{E_i}{E}\right)\sigma_{\rm e\ max} & (E \geq E_i). \end{cases} \tag{7b}$$

Substitute Eqs.(7a) and (7b) and Maxwellian EEDF into Eq.(6) and fit it using a function in the form $y = a \times {\rm e}^{bx^{\rm c}}$, then two empiric formulas will be generated as follows:

$$N_i = 2.2N\sigma_{\rm e\ max}{\rm e}^{-0.6507\varepsilon_i^{1.143}}, \tag{8a}$$

$$N_i = 2.8N\sigma_{\rm e\ max}\varepsilon_i{\rm e}^{-1.499\varepsilon_i^{0.8697}}. \tag{8b}$$

The above two formulas can be combined into a unified form: $N_i = KN\sigma_{\rm e\ max}\varepsilon_i^a{\rm e}^{-b\varepsilon_i^c}$, where the constants are listed in Table 5.

Table 5. Parameters of population calculation using step and hyperbolic functions.

step function				hyperbolic function			
K	a	b	c	K	a	b	c
2.2	0	0.6507	1.143	2.8	1	1.499	0.8697

Substituting the above general expression and $\varepsilon_i = \dfrac{E_i}{kT_{\rm e}}$ into an optically thin plasma spontaneous radiative formula

$$I_{ij} = \frac{h\upsilon_{ij}A_{ij}N_i}{4\pi}L, \tag{9}$$

where L is the plasma length which the light passes though, the expression for fitting $T_{\rm e}$ turns into the following form:

$$\ln\frac{I_{ij}\lambda_{ij}}{A_{ij}} = a\ln E_i - \frac{b}{(kT_{\rm e})^c}E_i^c + {\rm const.} \tag{10}$$

The fitting curves under 30 Pa utilizing Eq.(10) are presented in Fig.5. The curve in Fig.5(a) is fitted using a step function while in Fig.5(b) using a hyperbolic function. And the parameters in calculation are listed in Table 2. The values of $T_{\rm e}$ under various pressures are indicated in Table 6. Furthermore, the values of $T_{\rm e}$ calculated according to the PC theory[11] in low pressure glow discharges are also given in the last column of the same table so as to compare with the experimental results.

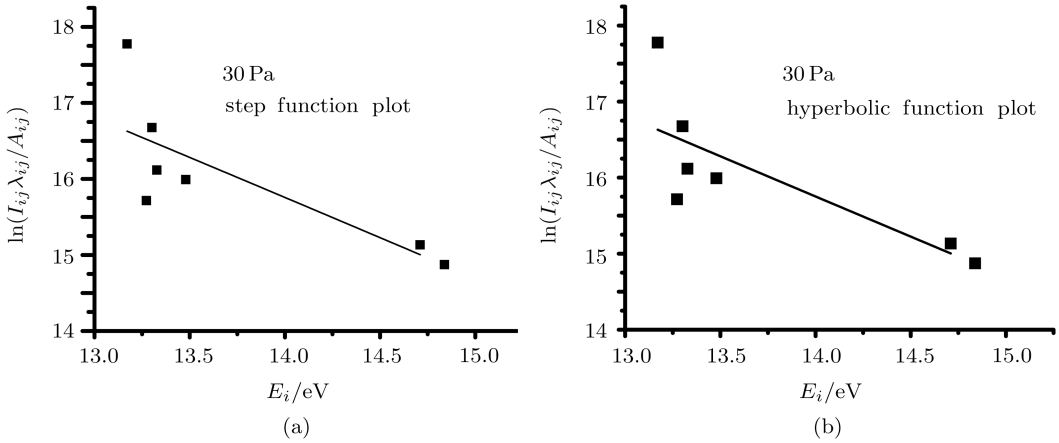


Fig.5. Fitting curves with a step function (a) and hyperbolic function (b).

Table 6. Fitted T_e using step and hyperbolic functions for approaching excited cross section, respectively.

pressure /Pa	step function			hyperbolic function			PC theory
	T_e/eV	R^2	Chi^2	T_e/eV	R^2	Chi^2	T_e/eV
10	3.915 ± 6.831	0.034	1.217	2.669 ± 6.659	0.034	1.217	2.26
15	2.119 ± 1.788	0.214	0.560	1.883 ± 1.801	0.214	0.559	2.09
20	1.836 ± 1.191	0.315	0.459	1.599 ± 1.200	0.316	0.559	1.98
22	1.575 ± 0.804	0.426	0.404	1.336 ± 0.805	0.427	0.403	1.95
25	1.360 ± 0.552	0.540	0.357	1.122 ± 0.545	0.541	0.356	1.91
28	1.233 ± 0.503	0.482	0.490	0.997 ± 0.492	0.483	0.489	1.87
30	1.024 ± 0.323	0.609	0.447	0.795 ± 0.308	0.609	0.446	1.85

3.4. Results analysis

Electron temperature calculated by four models in one experiment versus the pressure varying from 10 to 30 Pa is presented in Fig.6. The following points can be seen from the figure:

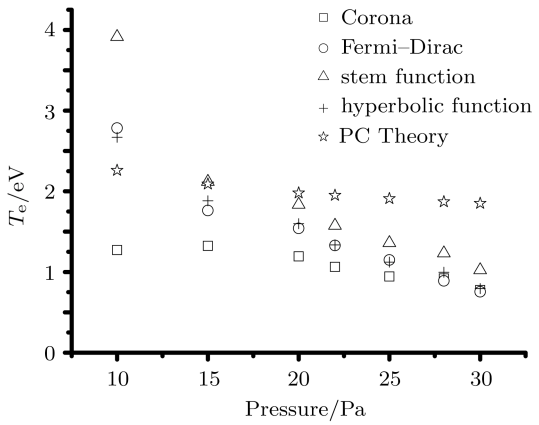


Fig.6. T_e versus pressures obtained separately by four models and PC theory.

1) The theoretical and experimental results both show that T_e decreases with increasing pressure. That is because of the average kinetic energy decreasing with reducing mean free path and more frequent collisions between electrons caused by raising up pressures. As a tendency of average kinetic energy, T_e also decreases.

2) Except T_e under 10 Pa, the results calculated by other methods are all less than those calculated from the PC discharge theory, because the wall-charge field influence of discharge chamber is not considered in the theory. The retarding action of wall-charge field on electrons becomes prominent under low pressures because of increasing the space-charge sheath in thickness near the wall, which can reduce the electron loss. Therefore, a lower electronic field is needed for maintaining the same discharge current, which gives less energy to electrons. However, relatively weak intensity of spectral lines under 10 Pa leads to more measurement errors and higher T_e.

3) T_e evaluated by the step function model is higher than those by using the other methods, because electron excited cross section is assumed to be unchangeable with its upper-level population. However, the actual cross section generally has a maximum with increasing upper-level population, and it decreases nearly exponentially. Using the step function for calculating T_e corresponds to the lowering of the slope of fitting curve, which results in a higher T_e.

4) T_e calculated by using the hyperbolic function is very close to that from the Fermi–Dirac model. It can be observed from Eqs.(1) and (10) that the curves for population versus upper level for the two models are basically the same in shape, indicating that although the two methods are based on different theories (the former acquires the densities in excited states according to a spontaneous radiation theory in a low pressure glow discharge, while the latter assumes the particles in an equilibrium plasma to obey the Fermi–Dirac model), they can all describe the features of emitted spectral lines in our plasma.

5) Results obtained from the corona model at low pressures are less than those from the other methods. One possible reason is that the states in our plasma have not reached the corona balance entirely due to less collisional frequency. Another reason may be the errors arising from the evaluation of the sum $\sum_{i>j} A_{ij}$.

6) Compared with T_e in Table 4, obtained by single probe, electron temperatures evaluated by spectro-

scopic diagnostics are relatively small. There are two reasons for the difference. On the one hand, strictly speaking, what the probe measures is the average electron kinetic energy in plasmas, which is traditionally named electron temperature denoted by T_e. However the result obtained by spectroscopy reflects electron energy in atom or ion excited levels and is termed the electron excitation temperature denoted by T_{exc}. According to the Griem's results,[2] T_e is equal to T_{exc} only when plasma is in a LTE state. Under general conditions, the two temperatures are not equal. Yanguas-Gil *et al*[12] have reported that T_{exc} in discharge plasmas at atmospheric pressure is lower than T_e, while the results obtained from DC glow plasmas at low pressures have not been reported yet. On the other hand, the assumption of Maxwellian EEDF dose not exactly hold true compared with the case of probe. The actual EEDF in our plasma deviates from Maxwellian distribution.[13] It is another reason why the results in the evaluated electron temperatures using two diagnostic methods are different.

4. Conclusion

In this article, we have made a comparison of four spectroscopic methods of determining electron temperature and presented their deduction and fitting process. Furthermore, electron temperature and errors are calculated using our optical emission spectroscopic data. From the comprehensive comparison among the results, we can conclude that the hyperbolic function model is the best method to calculate T_e in low pressure glow plasmas, although the results evaluated by the hyperbolic model and Fermi–Dirac model are almost the same. That is because the former has a sounder theoretical foundation of spontaneous radiation in low pressure glow discharges under the laboratory plasma environments, while the latter is the population model in an equilibrium plasma which deviates from the actual discharge conditions to a certain extent. So the hyperbolic function model with relatively simple assumptions is indeed successful in spectroscopically determining electron temperature in low pressure dc glow plasmas.

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