Journal of Quantitative Spectroscopy & Radiative Transfer 198 (2017) 93–103

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

Gas temperature determination of non-thermal atmospheric plasmas from the collisional broadening of argon atomic emission lines

A. Rodero, M.C. García*

Grupo de Física de Plasmas: Diagnosis, Modelos y Aplicaciones (FQM-136) Edificio A. Einstein (C-2), Campus de Rabanales. Universidad de Córdoba, 14071 Córdoba, Spain

ARTICLE INFO

Article history:
Received 14 March 2017
Revised 27 April 2017
Accepted 8 May 2017
Available online 9 May 2017

Keywords:
Plasma spectroscopy
Non-thermal plasmas
Gas temperature
Collisional broadening
Atomic emission spectroscopy

ABSTRACT

In this work we propose a new method allowing gas temperature determination in argon non-thermal plasma jets, based on the measurement of the collisional broadening of different argon atomic lines corresponding to transitions into both resonance levels s_2 and s_4 of the $3p^5 4s$ configuration. The method was developed for fourteen lines: Ar I 978.45, 935.42, 922.45, 852.14, 840.82, 826.45, 750.39 (corresponding to transitions falling to level s_2) and 965.77, 842.46, 810.37, 800.62, 751.46, 738.40, 727.29 nm (corresponding to transitions falling to level s_4). A carefully study of the relative importance of all broadening mechanisms to the whole profile for these lines, under a broad range of experimental conditions, revealed that for electron densities and gas temperature lower than 10^{15} cm^{-3} and 2000 K, the Stark and Doppler broadenings can be neglected in the method, but the van der Waals contribution should not be ever discarded for gas temperature determination. The gas temperature of a microwave non-thermal plasma jet was determined using nine of these lines. Results were consistent with each other, and with those obtained from the rotational temperature derived from OH ro-vibrational band. Also, the influence of the air entrance on the collisional broadening of the lines has been studied and the way the method should be modified to include this effect is indicated.

1. Introduction

In the two last decades, the development of cold plasma sources operating in the open atmosphere has noteworthy grown. Besides of simplicity of handing conferred by the atmospheric pressure condition, their low power consumption and their capacity to induce physical and chemical processes at relatively low gas temperatures are properties making them very attractive from an applied point of view. It is well known that the reactivity of these plasmas comes from their high energy electrons, while the ions and neutral species retain a *gas temperature* (or heavy particles temperature) T_g relatively cold.

In technological applications, such as those related to plasma surface treatments (thin film deposition, sterilization, surface functionalization…) or plasma treatment of liquids, a reliable determination of the gas temperature in the plasma could be crucial. But, to control this plasma characteristic parameter becomes particularly relevant when applying cold plasma technology directly on living human (and animal) cells, tissues and organs. In the last few years, a large variety of cold atmospheric plasma (CAP) sources for therapeutic uses in the medicine area [1–5] have been designed.

Optical Emission Spectroscopy (OES) techniques based on the analysis of molecular emission spectra are commonly used for gas temperature determination of plasmas sustained at atmospheric pressure. The rotational temperature derived from them is considered as a good estimation of the kinetic temperature of the plasma heavy particles due to the strong coupling between translational and rotational energy states under these high pressure conditions [6–13]. Nevertheless, the use of molecular emission spectroscopy is not always easy for gas temperature measurement in plasmas [14–17]. Overlapping of bands, rotational population distribution of levels having a non-Boltzmann nature, wake emission of rotational bands, among others, can make difficult to obtain reliable values of gas temperature. Also, some of these techniques have been shown to be poor sensitive for gas temperature determination in CAP conditions, near the room temperature [18].

Alternative OES methods for gas temperature determination in cold plasmas are then needed, and those based on the analysis of atomic lines profiles could be a good option. In this way, the *van der Waals* broadening of some argon atomic lines (broadening related to the plasma gas temperature, as we will show later) have been used for this purpose [19–22]. This technique is based

* Corresponding author.
E-mail address: fa1gamam@uco.es (M.C. García).

http://dx.doi.org/10.1016/j.jqsrt.2017.05.004
0022-4073/

on detection of argon atomic lines (Ar I 425.94, 522.13, 549.61 and 603.21 nm) not having resonance broadening (also related to T_g), but requires the use of additional techniques for simultaneous electron density determination, as these lines have a non negligible *Stark* broadening for electron densities above 10^{14} cm^{-3} which needs to be determined. Yubero et al. in [23] have proposed a way to circumvent this dependence on electron density considering pairs of these lines.

Recently Pipa et al. [18] have proposed a new method for gas temperature determination from the resonance broadening of some argon emission lines (Ar I 750.39, 826.45, 840.82, 852.14, 922.45 and 978.45 nm), corresponding to transitions into the resonance level s_2 (Paschen notations) of the $3p^5 4s$ configuration. This method sustains on three premises: (i) these lines have a strong resonance broadening related to the gas temperature; (ii) they have a negligible Stark broadening for electron densities under 10^{15} cm^{-3} (so, additional measurements of electron densities are not needed); and (iii) according to the authors's claim (supported on some references they cited), these lines have a *van der Waals* broadening that can be also neglected.

In the present work, we propose a new method allowing gas temperature determination in argon non-thermal plasma jets with $T_g < 2000$ K (so also in cold plasma jets), based on the measurement of the collisional broadening of different argon atomic lines, all of them corresponding to transitions into both resonance levels s_2 and s_4 of the $3p^5 4s$ configuration. We developed this method for fourteen different lines (so actually, we present fourteen different tools): Ar I 978.45, 935.42, 922.45, 852.14, 840.82, 826.45, 750.39 (corresponding to transitions falling to level s_2) and 965.77, 842.46, 810.37, 800.62, 751.46, 738.40, 727.29 nm (corresponding to transitions falling to level s_4). As a previous step, we have studied the relative importance of the different mechanisms causing the broadening of each of these lines emitted by the plasma, i.e. the relative contribution of the different broadening mechanisms to the whole line profile. Particularly, the relative importance of resonance and van der Waals broadenings have been determined in order to elucidate whether or not the van der Waals contribution could be neglected under some specific experimental conditions of electron density and gas temperature. We will demonstrate that this contribution should not be discarded under any T_g condition. Furthermore, when using these lines, the van der Waals contribution to the whole broadening could be especially critical in the determination of the gas temperature of CAPs (with T_g under 350 K).

The new methods we propose in this work have been applied to gas temperature determination of an argon microwave jet open to the air. The values of the temperatures obtained using them, have been compared to the rotational temperatures derived from the OH ro-vibrational bands for validation.

Cold argon plasma jets for both technological and medical uses are very common, as operation in a noble gas atmosphere yields the advantage of accurate control of (biologically or not) active species generation by admixture of oxygen or nitrogen as well as water vapor. Anyway, also similar methods using different atomic lines (helium, oxygen,...) could be also developed for plasmas operating in other gases.

2. Line broadening mechanisms

In plasmas generated at atmospheric pressure with no presence of magnetic fields, atoms emission is generally broadened due to different effects. The combination of Doppler and pressure broadenings (encompassing Stark, van der Waals and resonance broadenings), gives rise to an emitted line profile, that eventually can experiment additional broadening mechanisms (instrumental and self-absorption broadenings) during the detection process by the optical system. As a result, the line profile detected can be reasonably well fitted to a Voigt function in many cases.

Next, we will briefly describe these broadening mechanisms in order to review the plasma or optical system characteristic parameters determining each of them.

2.1. Collisional broadenings

Emitting atoms suffer frequent collisions with other atoms and ions in the plasma, which produces distortion of their energy levels. This is a mechanism leading to the so called *collisional or pressure broadening* of the emission lines. Depending on the nature of disturbing particles, there are different types of collisional broadenings: *van der Waals, resonance* and *Stark* broadenings.

The van der Waals (VDW) broadening is due to dipole moment induced by neutral atom perturbers in the instantaneous oscillating electric field of the excited emitter atom and generates line profiles with a Lorentzian shape with a FWHM W_W that, according to the Lindholm-Foley theory [24], is given (in nm) by

$$W_W = 8.18 \cdot 10^{-12} \lambda^2 \left(\alpha \langle \overline{R^2} \rangle\right)^{2/5} (T_g/\mu)^{3/10} N \tag{1}$$

where

$$\langle \overline{R^2} \rangle = \langle \overline{R_U^2} \rangle - \langle \overline{R_L^2} \rangle \tag{2}$$

is the difference of the squares of coordinate vectors (in a_0 units) of the upper and lower level of the transition, λ the wavelength of the observed line in nm, α is the polarizability of perturbers interacting with the excited radiator in cm^3, T_g is the temperature of the emitters (coincident with the gas temperature) in K, μ is the atom-perturber reduced mass in a.m.u., and N is the density of perturbers in cm^{-3}.

In the Coulomb approximation, $\langle \overline{R_i^2} \rangle$ for a specific line can be calculated from:

$$\langle \overline{R_i^2} \rangle = \frac{1}{2} n_i^{*2} \left[5 n_i^{*2} + 1 - 3 l_i (l_i + 1) \right] \tag{3}$$

being l_i the orbital angular momentum quantum number and n_i^* the effective quantum number, which can be obtained from the hydrogen approximation as

$$n_i^{*2} = \frac{E_H}{E_P - E_i} \tag{4}$$

where E_P is the ionization level of the radiating atom, E_H is the Rydberg constant and E_i is the excitation energy of the upper or lower level of the transition corresponding to the line.

Considering the ideal gas equation $N = P/K_B T_g$, the expression for the FWHM due to van der Waals broadening can be written as,

$$W_W(T_g) = \frac{C_W}{T_g^{0.7}} \, (\mathrm{nm}) \tag{5}$$

with C_W being determined by the type of gas in the discharge and the nature of the atom emitters:

$$C_W = \frac{8.18 \cdot 10^{-19} \lambda^2 \left(\alpha \langle \overline{R^2} \rangle\right)^{2/5} P}{k_B \mu^{3/10}} \quad \left(\mathrm{nm} \cdot \mathrm{K}^{7/10}\right) \tag{6}$$

For an argon plasma at atmospheric pressure, when considering the van der Waals broadening of argon atomic lines ($\mu = 19.97$ and $\alpha = 16.54 \cdot 10^{-25}$ cm^3), C_W can be written as

$$C_W = 7.5 \cdot 10^{-7} \lambda^2 \left(\langle \overline{R^2} \rangle \right)^{2/5} (\mathrm{nm} \cdot K^{7/10}) \tag{7}$$

In short, the van der Waals broadening is also characteristic for every atomic line emitted and it is related to the gas temperature in the plasma.