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Comment on "Diagnostics of 13.56 MHz RF sustained Ar-N₂ plasma by optical emission spectroscopy" [Eur. Phys. J. Appl. Phys. 45 (2009) 11002]

N. Sadeghi^{1,a} and F. J. Gordillo-Vazquez²

1- Laboratoire de Spectrométrie Physique, Université Joseph Fourier & CNRS, BP87,
38402 Saint Martin d'Hères, France & Laboratoire des Technologies de la Microélectronique,
CNRS, 17 rue des Martyrs, 38054 Grenoble Cedex 09, France

2- Instituto de Astrofísica de Andalucía, CSIC, P.O. Box 3004, 18080 Granada, Spain

Abstract:

Several important errors and misinterpretations present in a recent publication by Khan *et al* [Eur. Phys. J. Appl. Phys. **45** (2009) 11002] are pointed out and discussed. In particular, it is shown that the method used to calculate the rate coefficients for the electron impact excitation of $3p^54p$ and $3p^55p$ states of argon is incorrect and leads to unrealistically high rate coefficients.

^a Corresponding author, E-mail: Nader.Sadeghi@ujf-grenoble.fr

In a recent publication, hereafter referred as Ref. 1, Khan *et al* have used optical emission spectroscopy (OES) in a parallel plate RF discharge in argon-nitrogen mixture to characterize the plasma and to get information about the electron temperature, T_e and the population densities in the excited states of species present, namely Ar, N_2 , N_2^+ and N. The electron temperature has been deduced from the emission intensity of several argon lines, assuming a corona balance for the upper state of these lines. The purpose of this *comment* is to point out several important errors and misinterpretations present in this paper.

1- Determination of T_e

In 1, the electron temperature is deduced from the modified Boltzmann plot of emission intensities of six Ar lines, listed in Table 1. Eq. (5) used for this plot comes from the corona balance equation (1), assuming that the upper state i of each observed line is populated by electron impact excitation of ground state Ar atoms and depopulated by radiative decay. However, several errors have been made in determination of excitation rate coefficients, K_{1i} , in which the subscript 1 refers to the ground state of argon (K_{ji} in Eqs. (1) and (4) and f_{ji} in Eq. (2) of Ref. 1, must be replaced by K_{1i} and f_{1i} , respectively, as reported in the original paper of Gordillo-Vazquez² of which the section 3 of Ref. 1 is a copy). From Eq. (2) of Ref. 1, K_{1i} is proportional to the absorption oscillator strength f_{1i} of the transition $1 \rightarrow i$. However, as was pointed out by Fujimoto³, Eq. (17) of his paper, which relates the electron impact excitation cross-section to the optical oscillator strength f_{1i} , can be used only if the optical transition from the ground state to the excited state i is allowed. But optical transitions to the ground state from the upper levels of the all lines used in 1 are forbidden. States $3p_7$ for the 427.21 nm, $2p_2$ for the 727.29 nm, $2p_3$ for the 738.39 nm and $2p_5$ for the 751.46 nm lines are of even symmetry, like the ground state of argon and the $4d_6$ state, for the 693.76 nm line, has a total angular momentum, $J=0$, same as the ground state (level notations in Table 1 of Ref. 1 must be corrected⁴). It is therefore not possible to define f_{1i} values for transitions to these states.

To overcome the absence of the oscillator strength from the ground state to the upper states of the observed lines, authors of Ref. 1 have apparently used in Eq. (2) the oscillators strengths of the lines from these levels to the $1s_4$ state, which are lines as listed on their Table 1. This way of doing is absolutely wrong because the rate coefficients to be evaluated are for the excitation from the ground state of argon atom and not from the resonant $1s_4$ state. It is therefore not surprising that the excitation rates calculated from data reported by Khan *et al* in their paper are completely unrealistic.

As an example, we have calculated the excitation rate coefficient of the $3p_7$ state using the electron energy dependent optical excitation cross section $\sigma_{416}(E)$ of the 416.42 nm argon line, for which $3p_7$ is the upper state. $\sigma_{416}(E)$ was taken from Fig.5 of the publication by Tsurubuchi *et al* ⁵. $K_{li}(3p_7)$ at different electron temperatures are then deduced from the integral:

$$K_{li}(3p_7) = \frac{1}{b_{416}} \int_0^{\infty} \sigma_{416}(E) \cdot g(E) \cdot v(E) \cdot dE = \frac{1}{b_{416}} \cdot \frac{1}{\sqrt{m \cdot \pi}} \left(\frac{2}{kT_e} \right)^{3/2} \int_0^{\infty} \sigma_{416}(E) \cdot E \cdot \text{Exp}(-E / kT_e) \cdot dE$$

where $b_{416}=0.037$, the branching ratio of the 416.42 nm line is deduced by multiplying its transition probability⁴ by the radiative lifetime of the $3p_7$ state⁶, $g(E)$ is the normalized electron energy distribution function, assumed Maxwellian, $v(E)$ is the electron velocity and m its mass. It should be stressed that $\sigma_{416}(E)$ of Ref. 5 includes both direct and cascading excitations of the $3p_7$ states. However, at low electron energy, cascade contribution shouldn't be very important and in any case, $\sigma_{416}(E)$ can be considered as an upper limit. Fig. 1 shows our calculated $K_{li}(3p_7)$ for kT_e between 1 and 5 eV, together with the excitation rate coefficients obtained using Eq. (4) and $b_{ji}=15.3 \times 10^{-7}$ in Table 1. of Ref 1 (the scale of the coordinate in Fig. 4 of Ref. 1 is wrong by a factor of 10). The difference, about 10^4 at 1 eV to 10^5 at 5 eV, is enormous. In Table 1, we report K_{li} values calculated from Eq. (4) and b_{ji} in Table 1. of Ref 1, for different excited states considered in that work for $kT_e= 2$ eV. These

individual states excitation rate coefficients, ranging between 1 and $330 \times 10^{-9} \text{ cm}^3 \cdot \text{s}^{-1}$, are all much larger than the total excitation rate coefficient of argon at 2 eV, $K_{\text{ex}} = 6 \times 10^{-11} \text{ cm}^3 \cdot \text{s}^{-1}$, as reported in Ref. 7. All these arguments evidence that the method employed by Khan *et al* to calculate the excitation rate coefficients of the excited states of argon is wrong, so are the electron temperatures deduced from these incorrect data. The $\pm 10\%$ uncertainty attributed to T_e values in Fig. 5 of Ref. 1 is meaningless considering the very bad quality of the data point in their Fig. 3, from which T_e was deduced.

We should mention that the same wrong treatment has been used by this group for the determination of kT_e in neon-nitrogen plasma⁸. The excitation rate coefficients they calculate - as an example $1.26 \times 10^{-8} \text{ cm}^3 \cdot \text{s}^{-1}$ for the $3p [5/2]_3$ state (the upper level of the 640.22 nm line) at $kT_e = 2 \text{ eV}$ - are also unrealistic and several orders of magnitude higher than the known values.

2- Spectroscopic inconstancies

The assignment on Fig. 2 of Ref. 1 of different argon and nitrogen lines doesn't seem to be correct. In Fig. 2, the intensity of 427.21 nm line is unusually high compared to the other argon lines. According to the NIST data base⁹, the intensity of this line must be 1/3 of the intensity of the 420.07 nm line, which is totally absent in the spectrum shown in Fig.2. To our opinion, the peak assigned as 427.21 nm Ar line must be the maximum of the $\text{N}_2^+(\text{B}^2\Sigma; v'=0 \rightarrow \text{X}^2\Sigma; v'=1)$ band, whose origin is at 427.81 nm¹⁰. The 0-0 band of this transition at 391.44 nm is also present in Fig.2. Similarly, the upper level of the 667.72 nm argon line is the $2p_1$ state from which the 750.39 nm line is also originated. However, in the NIST data base⁹, the intensity of 750.39 nm line is 200 times larger than that of 667.72 nm line. The same ratio 200 also exists on transition probabilities of these lines⁴. Also, the intensity of 693.76 nm line must be 200 times smaller than that of the 696.54 line⁹. The weakness of these usually strong 750.39 and 696.54 nm lines in the spectrum of Fig. 2 reveals the misassignment of the peaks

at 667.7 and 693.76 nm to argon lines. A tentative explanation of the origin of these peaks in near infrared region of the spectrum could be the non zero transmission of the monochromator in the 2nd diffraction order of the grating. This idea is reinforced by the shape of the spectrum in this region that seems to be composed of molecular bands.

The same ambiguity exists for the 493.5 nm nitrogen line. According to the NIST data base⁹, this line must be about 4 to 5 times weaker than the 572.25 nm line, or any of the 742.36, 744.23 and 746.83 triplet lines, who all are absent in the spectrum of Fig. 2.

3- Concluding remarks

The above reported remarks reveals that the work presented by Khan *et al* is absolutely not reliable. Optical emission spectroscopy is a very simple and cost effective technique that can be very easily implemented. However, the recorded spectra need to be correctly analyzed. The absence of an atomic line, or a molecular band, can sometimes provide as much information than the presence of another ones.

Before copying equations from previous publications, the authors of a paper must first analyze the application domain of those equations and be ascertain that they can be applied to their work. They also must use the correct parameters, the oscillator strengths in the present case. Above all, authors must check if the numerical values they are reporting can be scientifically acceptable.

Finally, it must be pointed out that in the plasmas of argon nitrogen mixture, N₂(C) state is also very efficiently populated by the energy transfer reaction from argon metastable atoms¹¹, Reaction (R1) of Ref.1. Therefore, the contribution of this reaction to the observed intensity of the 2nd positive bands must be included in Eq. (9) of Ref. 1.

Upper state	3p₇	2p₁	4d₆	2p₂	2p₃	2p₅
Line (nm)	427.21	667.72	693.76	727.29	738.39	751.46
K_{li} (10⁻⁹ cm³.s⁻¹)	1.07	1.03	12.9	38	218	330

Table 1. Excitation rates at $kT_e=2$ eV of studied argon levels calculated with Eq. (4) and b_{ji} values of Table 1. of Ref. 1.

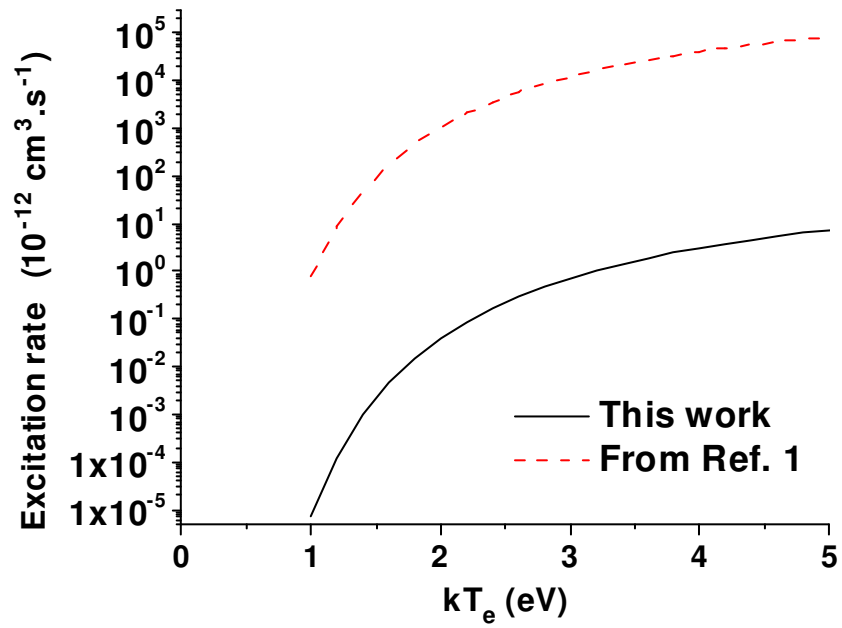


Fig. 1. Electron temperature dependence of the electron impact excitation rate of the $3p_7$ state from Ref. 1 (dashed line) and as calculated in this work (solid line).

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