Revista de Física Aplicada e Instrumentação, Vol. 6, nº 4, 1991

The relation between emission and optogalvanic signal intensities for argon transitions in hollow-cathode discharges

C. G. S. Costa, J. V. B. Gomide, A. Scalabrin
Instituto de Física Gleb Wataghin, UNICAMP, C. Postal 6165, 13081, Campinas, SP, Brasil

and

A. Mirage
Comissão Nacional de Energia Nuclear, Instituto de Pesquisas Energéticas e Nucleares, Caixa Postal 11049, São Paulo, 05499, SP, Brasil

Recebido em 27 de maio de 1992

Abstract We present the emission intensities compared to the optogalvanic signal magnitudes for neutral argon transitions in a hollow-cathode discharge, over the spectral range of 570-610 nm, measured in a continuous-wave regime. We show that there is a direct relation between the relative intensities of these spectra and note that this are possible because there is no lower metastable states involved in the observed transitions. Based on this correlation we derive an estimate for the electronic temperature in the discharge, in good agreement with data available in the literature.

1. Introduction

The optogalvanic effect (OGE) is the photoinduced change in a plasma impedance that takes place when the incident radiation frequency is resonant to any transition of atoms and molecules in the discharge. Although it has been widely used as a powerful spectroscopic tool, the environment of a discharge is so complex that the OGE can not be yet described by a general theoretical model. For an explanation of many interesting applications and a description of relevant attempts to establish quantitative understanding of the OGE, we refer to a recent review on the subject[1].

Partial financial support of CNPq, FAPESP and FINEP.

In the mechanistic model proposed by Keller, Engleman and Zalewski[2,3], the magnitude of the OGE can be correlated with the probability for absorption of laser radiation. According to their model, the magnitude ΔZ_{12} of the photoinduced plasma impedance change is supposed to be

$$\frac{\Delta Z_{12}}{I_{12}} \propto \lambda_{12}\, g_1\, f_{12} \cdot \exp\{-E_1/kT\}, \tag{1}$$

where I_{12} and λ_{12} are, respectively, the laser intensity and wavelength, and f_{12} is the oscillator strength (the f-value) of the considered transition. The product $\lambda \cdot f$ is proportional to the cross section for absorption of light at the peak center. Here, g_1 and E_1 are, respectively, the degeneracy and the energy of the initial lower state. It is assumed a Boltzmann distribution for the occupation of the atomic levels. This correlation was then verified for a large range of uranium transitions and most of the neon ones.

Based on this assumption, Keller, Engleman and Palmer[4] (from now on abbreviated as KE&P), pointed out that, under certain conditions, can also exist a direct proportionality between magnitudes of the optogalvanic signal (OGS) and the correspondent emission line intensities. In fact, the emission intensity F_{21} related to this transition can be written in a very convenient way,

$$F_{21} \propto \Phi(1/\lambda_{12})\, \lambda_{12}\, g_1\, f_{12} \cdot \exp\{-E_1/kT\}, \tag{2}$$

where the $\Phi(1/\lambda_{12})$ function is given by

$$\Phi(1/\lambda_{12}) = \frac{1}{(\lambda_{12})^4} \cdot \exp\left\{-\frac{1}{\lambda_{12}}\frac{hc}{kT}\right\}, \tag{3}$$

and contains all the extra factors $(1/\lambda_{12})$ that appear in the relation between Eq. (1) and (2). For small wavelength intervals ($\Delta\lambda/\lambda \leq 1\%$), the Φ-function can be regarded as constant and so KE&P expected to find a direct correlation between the OGS magnitude and the emission intensity. This hypothesis was successfully tested for the uranium transitions, within a range of $\Delta\lambda \approx 2.5$nm, disregarding some few exceptional transitions.

However, for calcium[5] and neon[3,4,6,7] there is not an agreement between the authors, about the validity of the above relation. Otherwise, Reddy *et al.*[8] have found that the OGS magnitudes are in accordance with the emission intensities for argon, in a pulsed regime. In this paper we investigate the correlation between emission and optogalvanic intensities for neutral argon transitions in a hollow-cathode lamp (HCL), in a continuous-wave (CW) regime experiment, and derive an estimate for the electronic temperature of the plasma.

2. Experimental

In our experiment we used a lamp with copper hollow-cathode, filled with a 7.9 Torr ultra-pure argon atmosphere. To perform the OGS measurements we directed the beam of a CW tunable dye laser (with Rhodamine 6G), optically pumped by an argon ion laser, through the hollow-cathode discharge. In order to avoid saturation effects in the impedance changes we limited the output power to 150mW. The discharge was maintained by a stabilized voltage power supply, working in the range of 200-300 VDC, connected to the lamp by a ballast resistor (R= [illegible] KΩ). The resonant OGS was monitored by a Lock-in Amplifier, modulating the laser amplitude with a mechanical chopper. The emission spectrum was obtained by a 0.85m double monochromator spectrometer SPEX 1402, also used for the dye laser wavelength calibration.

We used both spectroscopic techniques for several discharge current values. In the 570-610nm spectral range, the Ar-Cu lamp spectra presented only two relevant cathodic lines (Cu I 570.0nm and Cu I 578.2nm), thus the sample could be used to provide clear neutral argon transitions. The optogalvanic spectroscopy showed itself very sensitive, being possible to identify 46 Ar I lines, within 52 listed by Striganov and Odintsova[9] in this spectral range. Only those having emission intensities less or equal to 2 in a scale of 10,000 were not observed. In order to perform the desired comparison, we selected the relevant argon emission lines measured, identified in Table 1, which also includes the respective gf-values (derived from Ref. 10).

λ (nm)		LEVEL CLASSIFICATION		LEVEL ENERGY ($10^3 cm^{-1}$)		$g f$
		Lower	Upper	Lower	Upper	
1	574.0	4p [3/2] (1)	5d' [5/2]° (2)	106.09	123.51	0.0225
2	577.2	4p [3/2] (2)	5d' [5/2]° (3)	106.24	123.56	0.0073
3	580.2	4p [3/2] (2)	6d [1/2]° (1)	106.24	123.47	0.0067
4	583.4	4p [3/2] (2)	5d' [3/2]° (2)	106.24	123.37	0.0133
5	586.0	4p [1/2] (1)	6s' [1/2]° (1)	104.10	121.16	0.0044
6	588.3	4p [1/2] (1)	6s' [1/2]° (0)	104.10	121.10	0.0066
7	588.9	4p [5/2] (3)	7s [3/2]° (2)	105.46	122.44	0.0348
8	591.2	4p [1/2] (1)	4d' [3/2]° (1)	104.10	121.01	0.0165
9	592.9	4p [5/2] (2)	7s [3/2]° (1)	105.62	122.48	0.0174
10	594.3	4p [5/2] (2)	7s [3/2]° (2)	105.62	122.44	0.0050
11	598.7	4p [5/2] (3)	5d [7/2]° (3)	105.46	122.16	0.0049
12	599.9	4p [5/2] (2)	5d [5/2]° (2)	105.62	122.28	0.0040
13	602.5	4p' [3/2] (1)	7s' [1/2]° (1)	107.13	123.88	0.0153
14	603.2	4p [5/2] (3)	5d [7/2]° (4)	105.46	122.04	0.1208
15	604.3	4p [5/2] (2)	5d [7/2]° (3)	105.62	122.16	0.0586
16	605.3	4p [1/2] (1)	4d' [5/2]° (2)	104.10	120.62	0.0055
17	605.9	4p [1/2] (1)	4d' [3/2]° (2)	104.10	120.60	0.0117

Table 1: Identification of strong neutral argon emission lines observed in the range 570-610nm (gf-values also included). The classification is in a jl-coupling scheme, with primed notation referring to the Ar core coupling of $^2P^o_{1/2}$ and without prime to the coupling of $^2P^o_{3/2}$.

3. Results and discussion

By taking our measurements with the Ar-Cu lamp, we compared the emission intensities with the OGS magnitude (divided by the laser intensity) for neutral argon transitions over a spectral range of $\Delta\lambda \approx 40$nm, as shown in Figure 1. Both measurements were taken with $i = 11$mA in the HCL. The best choice for the normalization intensity was to take a central strong emission line (591.2nm), in order to minimize fluctuations introduced by large wavelength separations, once the Φ-function given by Eq. (3) is supposed to be constant in the interval $\Delta\lambda$. From Figure 1 we verify that the agreement is satisfied, within a factor of 2, for 14/17 transitions of the neutral argon, the only exceptions being the lines 588.9nm, 603.2nm, and 604.3nm.

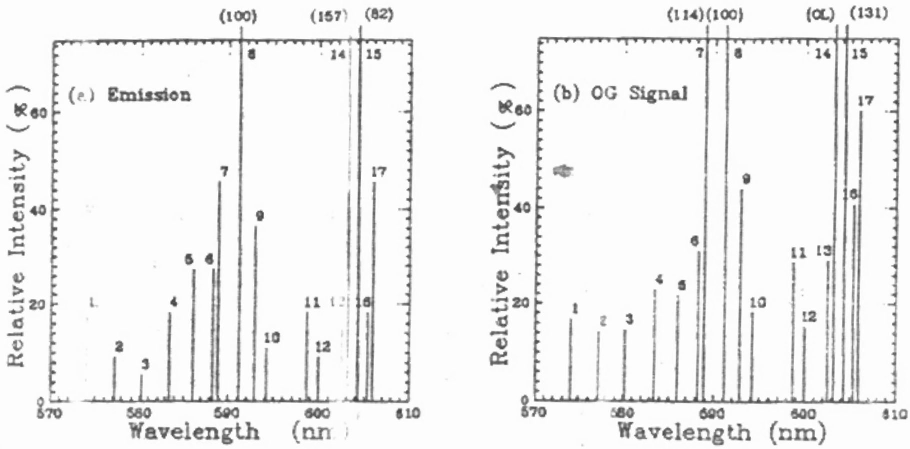

Fig. 1 – Comparison of (a) relative emission intensities with (b) relative OGS magnitudes (divided by the laser intensity) for argon transitions. Numbers identifying lines refer to Table 1. Lamp current: 11mA in both measurements. (OL) = Over Load, for intensity > 300%.

Althought the model described by Eq. (1), associating the OGS magnitude only to the population of the initial state has led to a controversy in the literature[11,12], it is very well suited for the uranium transitions, as have been observed experimentally[4]. The fact that it was not verified for calcium[5] and some neon transitions[3,4,6,7] is due to the presence of lower metastable levels in the proccess leading to the OGS.

As a matter of fact, Reddy *et al.*[8] claimed that the relative intensities of the spectral lines in optogalvanic effect is expected to be proportional to those in emission. They studied 300 lines in neon and almost 200 lines in argon, in the wavelength interval 410-670nm, using a pulsed laser source in order to analyse the temporal evolution of the OGS. They concluded that discrepancies between emission and optogalvanic spectra are due to the set of sampling parameters, as gate duration and delay time, when recording the time-dependent optogalvanic signal with a boxcar/gated integrator. This is not a problem when performing optogalvanic spectroscopy in a CW regime, as in our experiment. In this case, it is not difficult to take measurements and find a correspondence as shown in Figure 1.

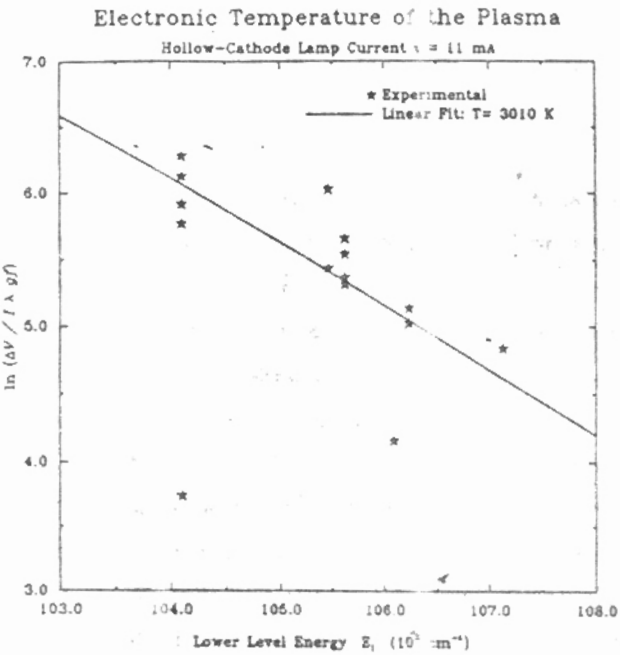

Fig. 2 - Linear interpolation of $\ln(\Delta V/I\ \lambda\ gf)$ against the lower level energy E_1 for neutral argon transitions. Energies, wavelegths and gf-values are from Table 1. Lamp current = 11mA; laser power ≈ 150 mW.

Now, coming back to Eq.(1) and assuming that the optogalvanic voltage change is given by $\Delta V_{12} = i\ \Delta Z_{12}$, where i is the lamp current, we can write

$$\frac{\Delta V_{12}}{I_{12}\lambda_{12}\ gf} = C \exp\{-E_1/kT\}, \tag{4}$$

with C as an arbitrary constant.

Using the gf-values and the lower level energy E_1 of the observed transitions, as listed in Table 1, we present in Figure 2 a linear interpolation to the plot of $\ln(\Delta V_{12}/I_{12}\lambda_{12}\ gf)$ against E_1. The slope $-1/kT$ of this line leads us to an estimate for the electronic temperature of the plasma in the hollow-cathode discharge, that resulted to be equal to 3010 K (at i = 11mA). The same plot obtained for i = 7.5 mA led to a value of 2710 K. It is noticeable that these values are in accordance with the ranges given by several authors in the literature: 1000 – 3000 K for Ben-Amar *et al.*[13]; 3000 K for Keller *et al.*[2,14]; 1100 – 3500 K for Zalewski *et al.*[3] and 3500 K for Drèze *et al.*[15].

4. Conclusions

The association of the OGS with the oscillator strength of the laser-resonant transition and also with the population of the lower level leads to a direct correlation of its magnitude with the correspondent emission intensity, provided the comparison is confined to a restricted spectral range. We have shown that the relation between optogalvanic and emission intensities works well for neutral argon transitions, in a CW regime experiment, even over a range of $\Delta\lambda \approx$ 40nm, counting only three exceptional lines.

There are several consequences on the verification of this quantitative relationship, now extended to the argon spectrum. First of all, it became clear that the direct KE&P correlation is not a privilege of cathodic materials. In addition, it seems that this correlation actually holds for argon atoms because there is no metastable states involved in the observed transitions, a condition not satisfied neither by neon nor by calcium lines, in the same spectral region. This conclusion must be reinforced, in further works, by extending the analysis to other elements and to different spectral ranges. Anyway, one can apply a detailed knowledge of the emission spectrum to perform an optogalvanic wavelength calibration. This will be an useful guide for taking optogalvanic measurements of several cathodic species, in argon filled hollow cathode lamps. Finally, the association postulated by Eq. (1) can lead to an estimate for the electronic temperature of the plasma in the hollow-cathode lamp, which is a relevant parameter used to describe the operating state of the discharge.

References

1. B. Barbieri, N. Beverini and A. Sasso, Rev. Mod. Phys., **62**, 603 (1990).

2. R. A. Keller, R. Engleman, Jr., and E. F. Zalewski, J. Opt. Soc. Am., **69**, 738 (1979).
3. E. F. Zalewski, R. A. Keller and R. Engleman, Jr., J. Chem. Phys., **70**, 1015 (1979).
4. R. A. Keller, R. Engleman, Jr., and B. A. Palmer, Appl. Opt., **19**, 836 (1980).
5. H.-A. Bachor, P. J. Manson and R. J. Sandeman, Opt. Comm., **43**, 337 (1982).
6. K. C. Smyth and P. K. Schenck, Chem. Phys. Lett., **55**, 466 (1978).
7. A. Sasso, M. Ciocca and E. Arimondo, J. Opt. Soc. Am., **B5**, 1418 (1988).
8. B. R. Reddy, P. Venkateswarlu, M. C. George, AIP Conf. Proc. (USA), **191**, 731 (1989); Opt. Comm., **75**, 267 (1990).
9. A. R. Striganov and G. A. Odintsova, *Table of spectral lines of atoms and ions.* (Energy, Moscou, 1982, in russian).
10. C. H. Corliss and W. R. Bozman, *Experimental transition probabilities for spectral lines of seventy elements.* (NBS Monograph 53, 1962).
11. N. S. Kopeika, Appl. Opt., **21**, 3989 (1982).
12. R. A. Keller and E. F. Zalewski, Appl. Opt., **21**, 3992 (1982).
13. A. Ben-Amar, G. Erez and R. Shuker, J. Appl. Phys., **54**, 3688 (1983)
14. R. A. Keller and E. F. Zalewski, Appl. Opt., **19**, 3301 (1980).
15. C. Drèze, Y. Demers and J. M. Gagné, J. Opt. Soc. Am., **72**, 912 (1982).

Resumo

Apresentamos a comparação das intensidades do espectro de emissão com as do sinal optogalvânico, medido em regime de bombeamento óptico contínuo, para transições do argônio neutro em uma descarga de catodo oco, abrangendo a região espectral de 570-610nm. Mostramos que existe uma correspondência entre as intensidades relativas destes espectros e notamos que este fato tornou-se possível uma vez que nenhuma das transições observadas envolve níveis inferiores metaestáveis. Baseados nesta correlação, derivamos uma estimativa para a temperatura eletrônica do plasma na descarga de catodo oco, compatível com dados apresentados na literatura.