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Modeling of glow discharge optical emission spectrometry: Calculation of the argon atomic optical emission spectrum

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Abstract

The optical emission spectrum of the argon atomic lines in a glow discharge is calculated, using a collisional–radiative model for argon, which was recently developed (A. Bogaerts et al., Collisional–radiative model for an argon glow discharge, J. Appl. Phys., vol. 84, No 1, 1998). It is shown that the lines corresponding to 4p → 4s transitions clearly dominate the spectrum. They are, however, not responsible for the characteristic visible light in the glow discharge, because they are lying between 700 and 1000 nm, which is mainly in the near infrared. The characteristic blue light of the glow discharge is caused by the lines corresponding to 5p → 4s transitions (lying in the blue–violet part of the spectrum). Beside these two most important line groups (the so-called 'red' and 'blue' lines) a large number of other lines are present, making the entire argon spectrum quite complex. The calculated spectrum is compared with experimental spectra from the literature, and excellent qualitative agreement is obtained.

The calculated spatial distributions of optical emission lines originating from low excited levels (i.e., 4p, 3d, 5s, 5p, 4d, 6s) show a maximum in the cathode glow, caused by fast argon ion and atom impact excitation, to these levels, and a second maximum in the beginning of the negative glow, due to electron impact excitation. The maximum in the cathode glow is very pronounced for lines originating from the 4p levels, which is in agreement with experimental observations. The higher excited levels are not populated by fast argon ion and atom impact excitation but only by electron impact excitation; hence, lines originating from these levels exhibit only a maximum in the beginning of the negative glow.

Keywords: Glow discharge; Optical emission spectrometry; Modeling; Argon

1. Introduction

Glow discharges are used in a large number of applications, ranging from the microelectronics industry, to the laser and light industry, the plasma display panel technology, and analytical chemistry. In the latter application, the material to be analyzed is used as the cathode of the glow discharge, which is sputter-bombarded by plasma species. The sputtered cathode atoms enter the plasma and can be ionized or excited, making the glow discharge useful in analytical chemistry as source for mass spectrometry (GDMS) and optical emission spectrometry (GD-OES) [1,2]. In practice, the coupling of a glow discharge with an optical spectrometer for GD-OES gives rise to optical emission spectra, i.e., intensities of spectral lines in a certain wavelength range. Of analytical importance are the spectral lines of elements from the material to be analyzed (cathode):

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the wavelengths indicate which elements are present in the sample, and the intensities of the spectral lines give information about their concentration in the sample. However, next to the spectral lines of analytically important elements, the spectra contain a large number of argon (plasma gas) lines. These can interfere with the analytical spectral lines when they have nearly the same wavelength. Indeed, the number density of argon atoms in the plasma is many orders of magnitude higher than the corresponding densities of sputtered atoms (i.e., at 1 torr: ca. 10^{16} cm^{-3} for argon compared with ca. 10^{12}–10^{13} cm^{-3} for sputtered atoms with a sample concentration of 100% (matrix element) [3,4]; for trace concentrations in the sample, the number densities in the plasma will be still lower). The intensities of argon spectral lines are therefore expected to be higher than the corresponding intensities of analytical spectral lines; hence the latter can be completely covered by the argon lines, so that the intensity of the line can no longer give accurate information about the sample concentration. On the other hand, it is reported (e.g., in Ref. [5]) that argon lines can be used as reference lines for GD-OES depth-profiling analysis. In both cases, i.e., when argon lines are interfering or when they are used as reference lines, accurate knowledge about the argon line spectrum is desirable. Moreover, information about the luminous intensities at different wavelengths can also be interesting for the light industry.

To achieve better insight in the argon atomic spectral lines and their intensities, we have recently developed a collisional–radiative model for argon, which describes the behavior of various argon atomic excited levels [6]. Sixty-five effective levels of the argon atom were considered, and the relevant processes taken into account were radiative decay, electron, fast argon ion and fast and thermal argon atom impact ionization, excitation and deexcitation between all the levels, electron–ion radiative recombination and electron–ion three-body recombination where the third body is an electron, fast argon ion or atom, or a thermal argon atom. Some additional loss processes were incorporated for the two metastable (i.e., 4s) levels, i.e., Penning ionization of sputtered atoms, two-body and three-body collisions with argon ground state atoms, collisions between two atoms in a metastable level, and diffusion and subsequent deexcitation at the walls.

Our model is an extension of the general model of Vlcek for argon plasmas [7], with a more detailed analysis of the two 4s metastable levels and with the incorporation of additional processes. Moreover, the electron energy distribution is calculated with a Monte Carlo model. Similarly, a Monte Carlo model was applied to simulate the behavior of fast argon ions and atoms in the cathode dark space, and to calculate fast ion and atom impact excitation and ionization. Finally, a very important advantage of this new model is that the input parameters are macroscopic quantities (voltage, current, pressure) which can easily be measured, whereas in previous collisional–radiative models, like [7], local values of the gas temperature, and the electron temperature and number density are required, which usually have to be obtained from plasma diagnostic measurements.

To the authors' knowledge, it is the first time that such an extensive collisional–radiative model has been developed for an analytical glow discharge, and that optical emission intensities are calculated in this explicit way. The model of Vlcek [7], on the other hand, has been applied earlier to analytical inductively coupled plasmas (ICPs) in pure argon [8,9], which were investigated experimentally in Refs. [10,11]. However, this model for the ICP has never been used to calculate optical emission intensities. Indeed, in Ref. [8], the objective was to clarify the population mechanisms leading to the departure from local thermodynamic equilibrium (LTE) in the ICP, and to verify the validity of the close-to-LTE concept which plays a key role in plasma diagnostics and in the interpretation of analytical measurements. In Ref. [9], the extent of the ionization–recombination non-equilibrium is studied at various locations in the ICP, together with the corresponding local rates of change in electron number density due to ionization and recombination, which are of basic importance for the characterization of particle transport in a plasma. Moreover, an extensive collisional–radiative model has also been developed recently by Vlcek for magnesium in an analytical argon ICP [12]. The reliability of this model was checked in Ref. [13], by comparison of the obtained numerical results with the corresponding measurements carried out in Refs. [14–17] under various conditions in analytical zones of the ICP. It was shown that the model

calculations explain consistently the mechanisms populating the excited states in magnesium atoms and ions.

As far as our collisional–radiative model for the argon glow discharge is concerned [6], typical results include the population profiles of the various excited levels and the relative contributions of different populating and depopulating processes, as was presented in Ref. [6]. It was found, among other results, that radiative decay between the various excited levels is very important as a populating and depopulating process. Therefore, and also because it is of great importance for glow discharges used as light sources and as excitation sources for GD-OES, the present paper deals with calculated optical emission spectra resulting from radiative decay between the various levels, as well as with the spatial distribution of the optical emission lines. These results can also be interesting for data interpretation of optical spectra in plasma diagnostical studies.

2. Description of the calculation procedure

The optical emission intensities are calculated as the product of the level population of the upper level and the Einstein transition probability for radiative decay to the lower level. This gives only relative intensities, but this is satisfactory at present for predicting the dominant lines in the spectrum. The level populations of the excited levels are calculated with the collisional–radiative model, including 65 effective levels and the different populating and depopulating processes mentioned above. We refer to Ref. [6] for more detailed information about the model set-up and the resulting calculated level populations. From the level populations of the effective levels, the populations of the individual excited levels are calculated based on their statistical weights, as described also in Ref. [6]. Only the spectral lines between 300 and 1000 nm are considered, which corresponds roughly to the visible region (i.e., the region which is most readily experimentally available) and is extended to 1000 nm, because the region between 700 and 1000 nm contains the most intense spectral lines (see below). The spectral line intensities of the following argon atomic (ArI) transitions were calculated (altogether more than 600 transitions are considered):

4p, 5p, 6p, 7p, 8p, 9p → 4s;
8p, 9p → 5s;
6s, 7s, 8s, 9s, 10s → 4p;
4d, 5d, 6d, 7d → 4p;
7p, 8p, 9p → 3d;
5f, 6f, 7f, 8f, 9f → 3d.

Other transitions are not included because they are either optically forbidden or they correspond to wavelengths below 300 nm or above 1000 nm (e.g. decay to 6s, 7s, 5p, 6p, 4d, 5d, etc.) [18]. The transition probabilities of most transitions are adopted from the calculations of Katsonis and Drawin (determined on the basis of intermediate and (j,K) coupling) [18]; only for the transition probabilities corresponding to the 4p → 4s and 5p → 4s transitions, which are known as the two most important groups of Ar atomic lines (i.e., the ‘red’ lines and ‘blue’ lines, respectively), is the set of values recommended by Wiese et al. [19] employed. The presently calculated optical emission spectrum contains only ArI (atomic) lines, although in practice, argon ionic lines (ArII) will also be present. However, these ArII lines cannot yet be included in the present calculations, because a collisional–radiative model for the argon ion, similar to the one for the argon atom, would be required to calculate the argon ion excited level populations.

3. Results and discussion

Fig. 1 presents the complete optical emission spectrum, calculated for 1 torr, 1000 V and 2 mA, at about 0.17 cm from the cathode (i.e., in the beginning of the negative glow, which is generally considered as the most luminous part of the discharge). It can be seen that the most intense spectral lines are situated around 800 nm; nearly all the lines lying between 700 and 1000 nm correspond to the 4p → 4s transitions (i.e., so-called ‘red’ lines). It is indeed generally known that these lines have the highest spectral intensities in a glow discharge [19–21]. The highest line observed in the present spectrum, i.e., at 811.53 nm, is often used for monitoring the argon $4s[3/2]_2$ metastable level population by atomic absorption because of its high intensity in a hollow cathode

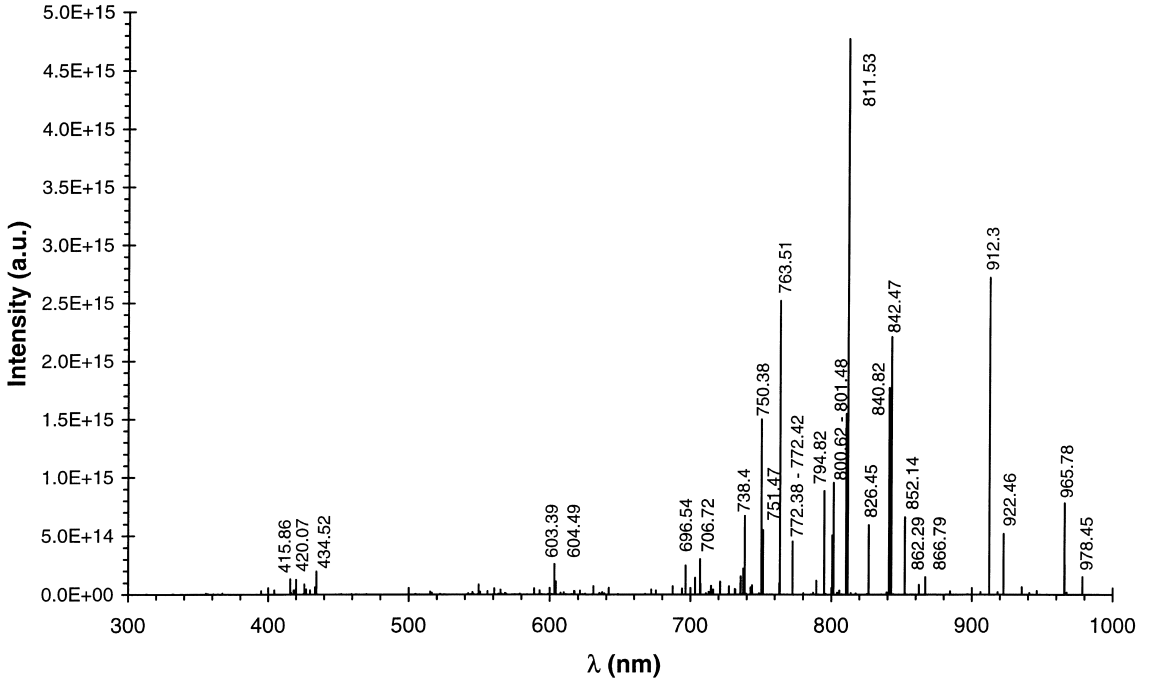

Fig. 1. Calculated argon atomic optical emission spectrum at 0.17 cm from the cathode (beginning of the negative glow), at 1000 V, 1 torr and 2 mA.

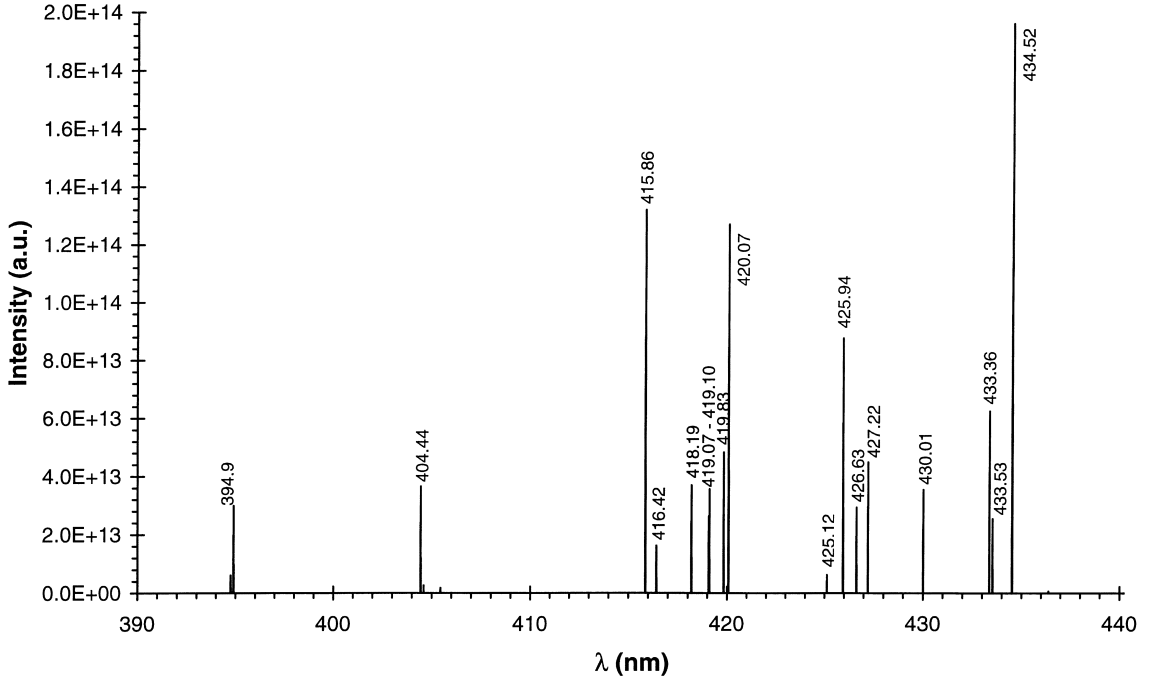

Fig. 2. Detail of the ‘blue’ lines (responsible for the characteristic blue glow in the glow discharge) in the calculated argon atomic optical emission spectrum, in the beginning of the negative glow, at 1000 V, 1 torr and 2 mA.

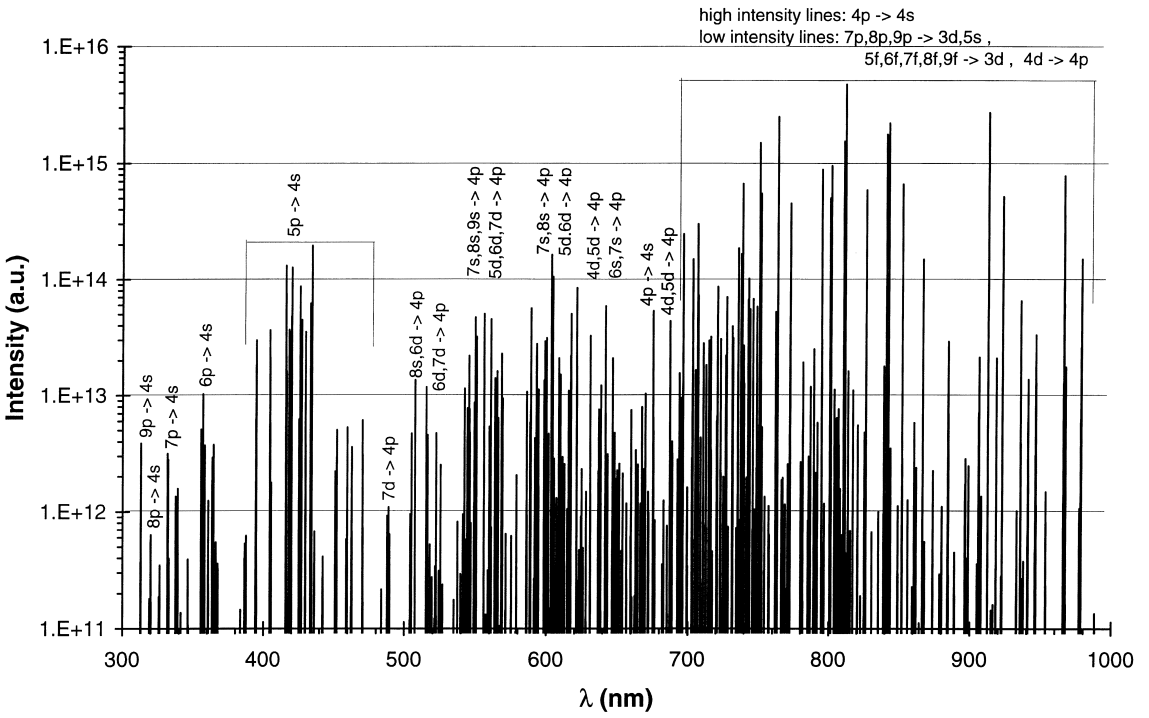

Fig. 3. Calculated argon atomic optical emission spectrum in the beginning of the negative glow, at 1000 V, 1 torr and 2 mA (logarithmic scale, showing the complexity of the spectrum).

glow discharge lamp [22–24]. These high intensity lines from 700 to 1000 nm are, however, not responsible for the visible glow in the glow discharge, because most of these lines are in the near infrared ($>$ 780 nm). Some other lines, of lower intensity, can however be observed in the spectrum of Fig. 1, i.e., at about 600 nm (5d $\rightarrow$ 4p lines, lying in the orange part of the spectrum) and at about 410–440 nm (5p $\rightarrow$ 4s lines, lying in the violet–blue region). It appears that the latter group of lines, in spite of their lower spectral intensities compared with the 'red' lines, are responsible for the typical glow (i.e., blue–violet) in an argon glow discharge. Because of their important role, Fig. 2 presents a detail of the optical emission spectrum at 0.17 cm from the cathode, i.e., the part containing the (so-called) 'blue' 5p $\rightarrow$ 4s lines. It can indeed be seen that there are quite a lot of lines lying close to each other in the blue and violet part of the spectrum, with still reasonably high intensities.

Besides these red and blue lines, the spectrum contains a large number of other spectral lines with variable intensities, as is illustrated by the emission spectrum on a logarithmic scale in Fig. 3. The transitions to which these spectral lines correspond are also indicated in the figure. It appears that the glow discharge emits quite a complicated spectrum (the ArII lines and lines corresponding to the sputtered cathode material are not even included here in the calculated spectrum), which is also experimentally observed. Indeed, as is always reported in review papers about glow discharge analytical spectrometry (e.g. [25,26]), one of the advantages of GDMS (glow discharge mass spectrometry) as an analytical technique compared with GD-OES (glow discharge optical emission spectrometry) is that the mass spectra are much simpler than the line-rich optical spectra, so that it suffers less from spectral interferences.

We have compared our calculated spectra with experimental argon spectra found in the literature. In Ref. [27], the intensities of a number of argon spectral lines, measured in two types of glow discharges (i.e., a 60-cycle a.c. glow discharge at a current of 60 mA and a pressure of 3 torr, and a hollow cathode glow discharge at a current of 150 mA and a pressure of 1 torr)

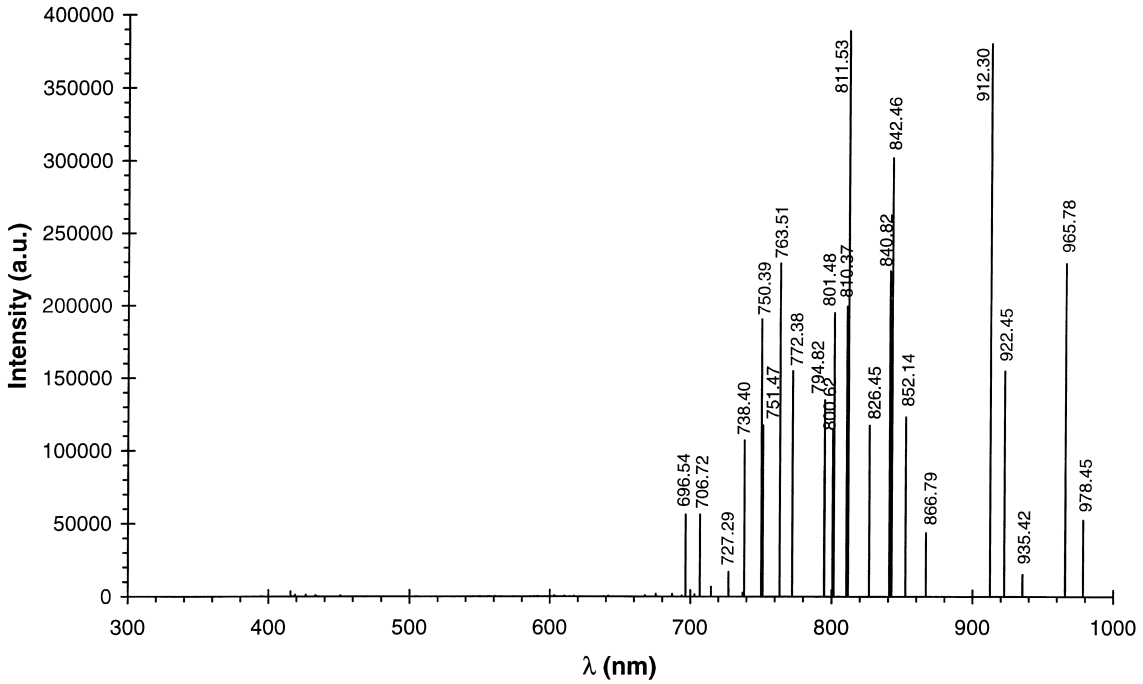

Fig. 4. Experimental argon atomic optical emission spectrum, measured in a hollow cathode glow discharge at a current of 150 mA and a pressure of 1 torr [27].

are tabulated. Exact comparison is not possible, due to different discharge conditions and cell geometries; moreover, it is not mentioned in Ref. [27] at which position the spectral line intensities were recorded, but probably the tabulated values are integrated over the entire discharge region. We have plotted these tabulated spectral intensities in both glow discharge sources, and the results are shown in Figs 4 and 5. Fig. 4 illustrates the complete spectrum measured for the hollow cathode discharge. It can be seen that the so-called 'red lines' are dominant in the spectrum, which is in excellent correspondence with our calculated results (Fig. 1). In the a.c. glow discharge, no lines with wavelengths larger than 900 nm were recorded, but the other line intensities were also very similar to our calculated results. Fig. 5 shows a detail of the region between 390 and 440 nm, which can be compared directly with our calculated spectrum in Fig. 2. Again very good agreement is reached. Indeed, comparing Figs 1, and 4 and Figs 2, and 5 tells us that the relative intensities of the various lines in our calculated spectrum are almost exactly reflected in the experimental spectra. There are only a few exceptions. From Figs 1, and 4 it follows that the intensity of the calculated 772.38 nm line is somewhat lower than in the experimental spectrum; this is also true for the groups of lines between 826.45 and 978.45 nm which are somewhat lower in intensity compared with the other 'red lines' (e.g., the 811.53 nm line), but within this group the relative intensities do agree very well with the experimental values. From Figs 2, and 5 it can be deduced that the calculated intensity of the 420.07 nm line is slightly lower than the experimental value, and the reverse is true for the 434.52 nm line. Moreover, the lines at 419.07 and 419.10 nm do not seem to be recorded in the experimental spectrum whereas they are present in the calculated spectrum.

However, beside these few exceptions, the calculated and experimental relative spectral line intensities are very similar to each other, in spite of the different discharge conditions of the experimental and calculated situations (it should be mentioned that both experimental spectra exhibit also such differences) and also in spite of possible uncertainties in the transition probabilities and in some cross sections

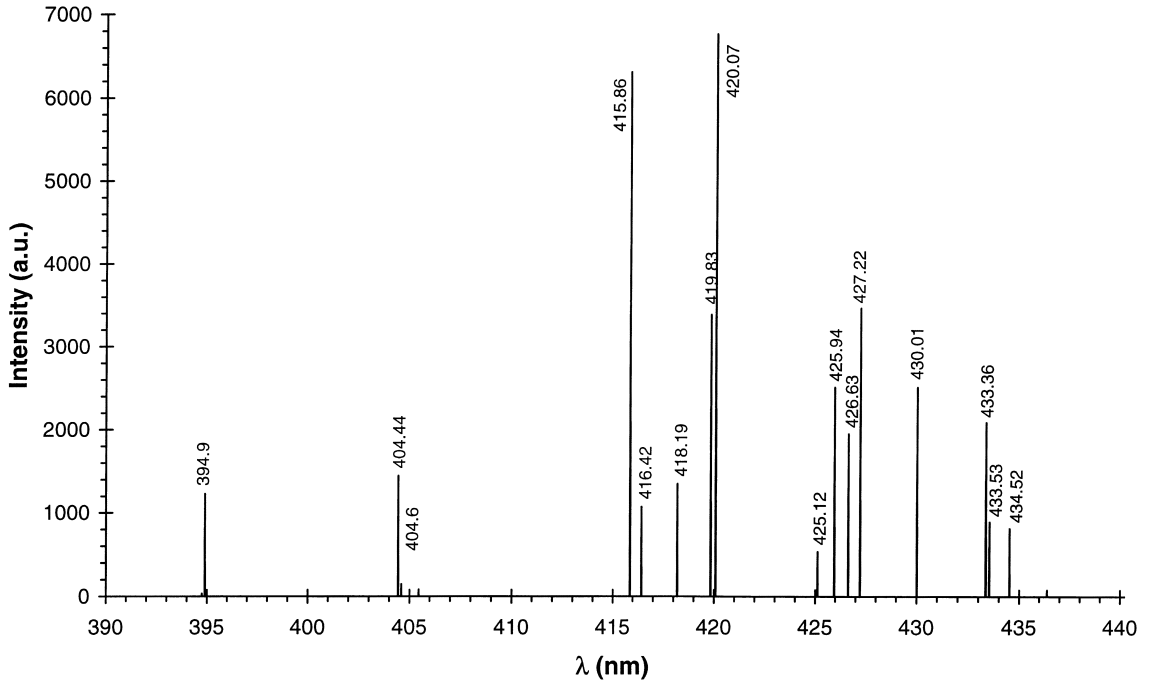

Fig. 5. Experimental argon atomic optical emission spectrum (detail of the 'blue' lines), measured in a 60 cycle a.c. glow discharge at a current of 60 mA and a pressure of 3 torr [27].

used in our collisional–radiative model. Indeed, variations in these input data were found to affect the spectral line intensities to some extent, but the general trend in the optical emission spectrum remains unchanged. The excellent agreement between calculated and experimental results tells us that our present model can generally be considered reliable and that it presents a realistic picture of the glow discharge.

We have not only calculated the emission spectrum at 0.17 cm from the cathode (in the beginning of the negative glow), but also at other locations, and the relative intensities of the spectrum remained more or less the same; only the absolute values decreased further away from the cathode (further in the negative glow). Therefore, the spectra at these other locations are not presented here. Closer to the cathode (in the cathode dark space), however, the relative intensities did change more clearly: spectral lines originating from high excited levels decreased in intensity, whereas spectral lines originating from lower excited levels (especially the 4p → 4s lines) first decreased to a local minimum and then became higher in intensity. This is attributed to the fact that these low levels can be populated by fast argon ion and atom impact excitation from the ground state, which becomes unimportant for the higher excited levels, since too high excitation energies would be required. Because the latter processes are only important close to the cathode where the argon ions and atoms can reach rather high energies, the level populations of these low excited levels reach a maximum close to the cathode beside the (smaller) maximum in the beginning of the negative glow (as was calculated in Ref. [6]), and this is also reflected in the spectral lines originating from these levels, whereas spectral lines coming from the higher levels do not exhibit this maximum close to the cathode.

This can also be observed in Fig. 6, where the calculated optical emission profiles of several lines (which are representative for most of the other lines) are presented, going from cathode ($z = 0$) to the end of the glow discharge cell ($z = 2$ cm). The 811.53 nm line (no. 1, whose intensity was decreased 100 times to fit in the figure, and which originates from a 4p level) exhibits a pronounced peak close to the cathode and

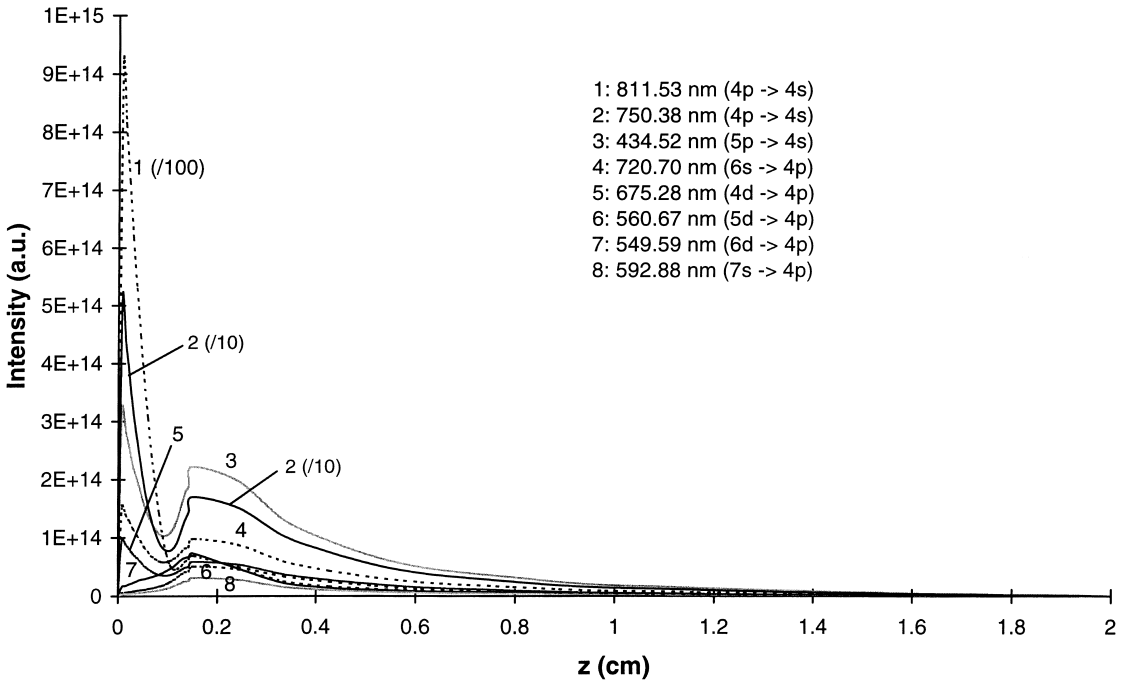

Fig. 6. Calculated argon atomic optical emission profiles, for some typical, representative spectral lines, at 1000 V, 1 torr and 2 mA.

only a very small peak in the beginning of the negative glow. The same is true for the 750.38 nm line (no. 2, whose intensity was decreased 10 times to fit in the figure) which arises also from a 4p level. The difference between cathode glow peak and negative glow peak is, however, not so pronounced here as for the 811.53 nm line, because it originates from a higher 4p level (i.e., 4p′ $[1/2]_0$ at 13.48 eV for the 750.38 nm line compared with 4p $[5/2]_3$ at 13.12 eV for the 811.53 nm line), which is not so efficiently excited by fast argon ion and atom impact excitation due to its higher excitation energy. This is in excellent agreement with Ref. [20], where the spatial distributions of different argon optical emission lines were measured in a direct current glow discharge at 0.25 to 8 mA and 0.27 mbar and where it was shown that the 811.5 nm line exhibited a very distinct peak in the cathode glow and almost no peak in the negative glow while the 750.3 nm line showed both a peak in the cathode glow and in the beginning of the negative glow. Also lines 3, 4 and 5, which arise from a 5p, 6s and 4d level, respectively, exhibit a peak in the cathode glow, but it is only slightly higher than the peak in the beginning of the negative glow, because excitation by fast argon ion and atom impact becomes gradually less efficient. The other optical emission lines presented in this figure (i.e., lines 6, 7 and 8), do not show any peak in the cathode glow at all, because they originate from too high levels which can no longer be populated by fast argon ion and atom impact excitation.

From Fig. 6, it can also be deduced that line no. 3, corresponding to a 5p → 4s transition (one of the ‘blue’ lines) is a factor of 10–100 lower than the ‘red’ lines, but it is still higher than the other lines, which corresponds well with experimental findings that the lines corresponding to the 4p → 4s and 5p → 4s transitions are the most important ones in the argon spectrum. Finally, it can be seen that line no. 7, which originates from a 6d level (i.e., the highest excited level included in this figure) drops off somewhat more rapidly after its maximum in the negative glow. This behavior is characteristic for the transitions originating from the higher excited levels. The reason for this more rapid drop-off is that the electron energy, which decreases in the negative glow because the electrons lose energy by collisions, will no longer be efficient enough to populate the

highly excited levels. Hence, the level populations of these higher excited levels, and therefore also the optical emission profiles of lines originating from these levels, drop off more rapidly after the maximum in the beginning of the negative glow.

4. Conclusion

The optical emission spectrum and the spatial distribution of optical emission lines of argon atoms in a glow discharge have been calculated using a recently developed collisional–radiative model for argon [6]. Indeed, the product of the level populations of the various excited argon atomic levels calculated with this model, and the Einstein transition probabilities for radiative decay from these levels to lower levels, yields the argon atomic optical emission spectrum. The present paper shows that the most intense lines in the emission spectrum are situated between 700 and 1000 nm, i.e., the so-called 'red' lines corresponding to the 4p → 4s transitions. These lines are not responsible for the characteristic, visible glow in the glow discharge, because most of them are lying in the near infrared. The color of the argon glow discharge (blue–violet) is determined by the spectral lines corresponding to the 5p → 4s transitions, which are a factor 10–30 less intense than the 'red' lines but are still of considerable intensity. These lines are indeed situated in the violet–blue part of the visible region and are generally called the 'blue' lines. Beside these two most important groups of spectral lines, the spectrum contains a large number of other argon lines with variable intensities, making the glow discharge spectrum rather complicated. The calculated spectrum is compared with experimental spectra found in the literature, and the calculated and experimental relative intensities of the various spectral lines were found to be in excellent agreement.

Finally, the spatial distribution of some spectral lines was calculated. It was shown that lines originating from low excited levels exhibit a pronounced maximum close to the cathode (in the cathode glow), caused by fast argon ion and atom impact excitation of the levels, and a second maximum in the beginning of the negative glow due to electron impact excitation of the levels. The spectral lines originating from higher excited levels, which cannot be populated by fast argon ion and atom impact excitation, do not show such a peak in the cathode glow but they are characterized by a peak in the negative glow. This behavior is also in satisfactory agreement with recent experimental observations.

The present results are important for obtaining better insight and improving the performance of glow discharges used as light sources and as spectroscopic sources for optical emission spectrometry. Moreover, they can be extremely useful for data interpretation of optical spectra in plasma diagnostic studies.

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References

[1] R.K. Marcus (Ed.), Glow Discharge Spectroscopies, Plenum Press, New York, 1993.
[2] R. Payling, D. Jones, A. Bengtson, Glow Discharge Optical Emission Spectrometry, Wiley, Chichester, 1997.
[3] A. Bogaerts, R. Gijbels, J. Appl. Phys. 79 (1996) 1279.
[4] A. Bogaerts, R. Gijbels, Anal. Chem. 68 (1996) 2676.
[5] A. Bengtson, A. Eklund, F. Präßler, Fresenius J. Anal. Chem. 355 (1996) 836.
[6] A. Bogaerts, R. Gijbels, J. Vlcek, Collisional–radiative model for an argon glow discharge, J. Appl. Phys., 84(1) (1998).
[7] J. Vlcek, J. Phys. D: Appl. Phys. 22 (1989) 623.
[8] J. Vlcek, V. Pelikan, J. Phys. D: Appl. Phys. 24 (1991) 309.
[9] J. Vlcek, V. Pelikan, Spectrochim. Acta B 47 (1992) 681.
[10] S. Nowak, J.A.M. van der Mullen, D.C. Schram, Spectrochim. Acta B 43 (1988) 1235.
[11] T. Hasegawa, T. Haraguchi, Spectrochim. Acta B 40 (1985) 1505.
[12] J. Vlcek, Spectrochim. Acta B 52 (1997) 599.
[13] J. Vlcek, L. Forejt, J.A.M. van der Mullen, Spectrochim. Acta B 52 (1997) 609.

[14] B.L. Caughlin, M.W. Blades, Spectrochim. Acta B 39 (1984) 1583.
[15] J.A.M. van der Mullen, I.J.M.M. Raaijmakers, A.C.A.P. van Lammeren, D.C. Schram, B. van der Sijde, H.J.W. Schenkelaars, Spectrochim. Acta B 42 (1987) 1039.
[16] T. Hasegawa, T. Haraguchi, Anal. Chem. 59 (1987) 2789.
[17] L.L. Burton, M.W. Blades, Spectrochim. Acta B 46 (1991) 819.
[18] K. Katsonis, H.W. Drawin, J. Quant. Spectrosc. Radiat. Transfer 23 (1980) 1.
[19] W.L. Wiese, J.W. Brault, K. Danzmann, V. Helbig, M. Kock, Phys. Rev. A 39 (1989) 2461.
[20] K. Rozsa, A. Gallagher, Z. Donko, Phys. Rev. E 52 (1995) 913.
[21] Z.M. Jelenak, Z.B. Velikic, J.V. Bozin, Lj.Z. Petrovic, B.M. Jelenkovic, Phys. Rev. E 47 (1993) 3566.
[22] J.H. Kolts, D.W. Setser, J. Chem. Phys. 68 (1978) 4848.
[23] R.L. Smith, D. Serxner, K.R. Hess, Anal. Chem. 61 (1989) 1103.
[24] M.K. Levy, D. Serxner, A.D. Angstadt, R.L. Smith, K.R. Hess, Spectrochim. Acta B 46 (1991) 253.
[25] W.W. Harrison, K.R. Hess, R.K. Marcus, F.L. King, Anal. Chem. 58 (1986) 341A.
[26] W.W. Harrison, C.M. Barshick, J.A. Klingler, P.H. Ratliff, Y. Mei, Anal. Chem. 62 (1990) 943A.
[27] D.E. Gray, American Institute of Physics Handbook, 3rd ed., McGraw Hill, New York, 1972.