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A Study of Deviation from Local Thermodynamic Equilibrium in Thermal Plasmas by Optical Emission Spectroscopy

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A fast, accurate and comprehensive optical emission spectroscopic set-up has been employed to investigate the deviation from local thermodynamic equilibrium in a 75- ampere argon plasma arc. The H_β and H_α lines of hydrogen were monitored with a spectrograph while an Ar I line and its neighbouring continuum were simultaneously monitored with a monochromator. The electron number densities calculated from Stark-broadened H_β and H_α lines of hydrogen were compared with those derived from absolute intensity measurements of the 7635 Å Ar I line. The H_α line showed an order-of-magnitude higher number density than LTE measurements; the H_α results are generally known to be inaccurate because this line is self-absorbing and its refined Stark-broadening parameters have not been calculated. The H_β line is usually the first choice for Stark-broadening calculations; its theory is well developed, and results are expected to be accurate within 10%. Results from the H_β line turned out to be about 4 times higher than LTE results. This difference is attributed to two possible reasons: first, the strong Ar I line also suffers from self-absorption and second, there may be a considerable deviation from LTE.

Key words: Local thermodynamic equilibrium, Plasma arcs, Emission spectroscopy.

Introduction

The concept of Local Thermodynamic Equilibrium (LTE) is a very powerful one and several researchers (Farmer and Haddad 1984; Cram *et al* 1988; Bakshi and Kearney 1989) have investigated deviations from LTE in thermal plasma arcs. When LTE prevails(Holtgreven 1968; Fauchais *et al* 1979) we have one temperature T_{LTE} for all present species (electrons, ions, atoms) and the description of the plasma is greatly simplified.

In this paper, a fast, accurate and comprehensive optical emission spectroscopic set-up has been employed to investigate the deviation from local thermodynamic equilibrium in a 75- ampere argon plasma arc. The H_β and H_α lines of hydrogen are monitored with a spectrograph while an Ar I line and its neighbouring continuum are simultaneously monitored with a monochromator. The electron number densities calculated from Stark-broadened H_β and H_α lines of hydrogen are compared with those derived from absolute intensity measurements of the 7635 Å Ar I line (Transition 4s $[3/2]^0_2$ - 4p $[3/2]_2$).

When LTE prevails, a common temperature T_{LTE} describes the Maxwell-Boltzmann velocity distribution for all the species in the plasma and the Boltzmann distribution of excited states of the atoms with respect to the ground state. In LTE, a number of equations are simultaneously valid. These include Saha Equation, Dalton Law or Equation of State, Charge Equilibrium, and Boltzmann's Distribution Law with respect to the ground state.

The following equation, however, is independent of the assumption of LTE. It relates line emission coefficients (Holtgreven 1968; Boulos *et al* 1989) to temperature (or emissivity to population density n_s of the upper energy level s):

$$\varepsilon_L = \frac{1}{4\pi}\, h\nu A_t^s n_s = \frac{1}{4\pi}\, h\nu A_t^s .\, n_o \frac{g_s}{Z_0} \exp(-E_s/kT) .. \quad (1)$$

where A_t^s is the probability of transition (sec^{-1}) from level s to t, n_s is the number density of level s, n_0 is the atomic number density (m^{-3}), g_s is the degeneracy, Z_0 is the partition function of atoms, E_s is the upper energy level (joules), and T is the temperature (°K).

After measuring line emission coefficient ε_l by emission spectroscopy, the above mentioned equations can be used to calculate LTE values of temperature T, atomic number density n_0, and electron number density n_e. These values of n_e, which critically depend upon the assumption of LTE, may then be compared with those derived separately from another

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method which is essentially independent of the assumption of LTE to indicate how closely LTE is approximated. If LTE exists, these two number densities should be the same. When they start differing from each other, deviation from LTE is indicated. In a truly collision dominated plasma, however, LTE is achieved because the inelastic collision rate between electrons and atoms exceeds that of radiation loss.

A popular means (Huddlestone and Leonard 1965; Holtgreven 1968) for determining electron densities, without dependence on the assumption of LTE, is the use of Stark broadening. This is principally a density effect and does not sensitively depend upon either temperature or electron velocity distribution. Since broadening effects are strongest for atoms showing linear Stark effect, hydrogen lines exhibit the strongest broadening. The Stark broadening measurements, therefore, will yield reliable electron densities even when the existence of LTE is doubtful.

In order to observe deviation of the plasma from LTE, a small amount of 1% hydrogen (because higher amounts can easily change the heat conductivity and temperature characteristics of the arc) may be admixtured to the plasma. As a first step, one spectral line (7635 Å, Transition $4s\,[3/2]^0_2 - 4p\,[3/2]_2$) of the constituent gas and its neighbouring continuum may be recorded on the monochromator-photomultipliers combination and the Stark-broadened β-line (4861 Å) of the hydrogen Balmer series may be simultaneously recorded using the Spectrograph-OMA combination. Immediately afterwards, the Stark-broadened α-line (6563 Å) of hydrogen Balmer series may be recorded. From the measured half-widths of these Stark-Broadened Balmer-lines, electron number densities may be computed with the aid of tabulated profiles (Griem 1964). These tabulated profiles, which are one half of the symmetrical profiles, are presented as function $S(\alpha)$ versus α; α, a reduced wavelength distance, is given by:

$$\alpha = \frac{\Delta\lambda}{F_0} \quad \text{..........} \quad (2)$$

where $\Delta\lambda$ is the distance from the centre of the spectral line, and F_0 (the "Holtsmark field strength") is given by:

$$F_0 = 1.25\times10^{-9}\, N_e^{(2/3)} \quad \text{..........} \quad (3)$$

The tabulated profiles are normalized such that:

$$\int_{-\infty}^{\infty} S(\alpha)\,.\,d\alpha = 1 \quad \text{..........} \quad (4)$$

For our application, however, a knowledge of the complete profile as a function of density is not required; only a relationship between (full) half-width and electron density is desired and follows from the above relations as:

$$\Delta\lambda_{1/2} = 2..50\times10^{-9}\,.\,\alpha_{1/2}\,.\,n_e^{(2/3)} \quad \text{..........} \quad (5)$$

The theoretical (half) half-width $\alpha_{1/2}$ (the value of α at which $S(\alpha)$ is at one-half of its maximum value), however, has to be obtained from the tabulated profiles first.

The number density, n_e, resulting from Stark broadening data may then be compared with that resulting from LTE calculations via the line emission coefficient, ε_L, of the measured spectral line of the constituent gas. The said comparison will indicate the extent of deviation of the plasma from LTE (T_e 9,000 K).

Experimental

The fully-automated, fast, accurate and comprehensive emission spectroscopic set-up (Akbar; Etemadi and Akbar 1990; Akbar and Etemadi 1991) employed for this experiment, is shown in Fig. 1 for ready reference.

For this investigations, an argon arc at 1 atmosphere with 13 mm electrode gap spacing was employed. The cathode material was 1% thoriated tungsten and pointed to 60° angle while the anode material was copper. The optical data was integrated for a 15 ms photodiode exposure-time. The detector temperature was maintained at 0°C with the help of a thermo-electric cooler assembly on which the photodiodes are mounted. The widths of entrance slits of the spectrograph and the monochromator were set at 10 μm and 60 μm respectively. The two PMTs, for line and continuum, were operated at 0.977 KV and 0.935 KV respectively.

In order to investigate the equilibrium state of the plasma, a small amount of hydrogen (1%) was admixtured to the 75 A argon arc. Radial scans of the arc were performed 2 mm below the cathode tip; each scan comprised 100 radial points and a step size of 0.1 mm. First, the Ar I line at 7635 Å and its neighbouring continuum were monitored with the monochromator and the Stark-broadened H_β line (4861 Å) of the hydrogen Balmer series was simultaneously recorded with the OMA. Second, the stark-broadened H_α line (6563 Å) of hydrogen Balmer series was recorded. Figure 2 shows the profile of the strong Ar I line at 7635 Å, as recorded with the emission spectroscopic set-up. Figure 3 shows the arc's emission spectrum between 4700 and 5050 Å wherein the characteristic hump of the H_β line (centre frequency 4861 Å) is discernable between 4825 and 4930 Å. Figure 4 shows a three dimensional radial scan of the H_β line (typically 40 Å wide), as recorded with the spectrograph-OMA combination. Although the general shape of the H_α line is visible, the characteristic dip in the middle has been obscured by the strong singly-ionized Ar lines (4848, 4866, 4880, 4889, and 4905 Å) riding atop the relatively weak H_β line. Figure 5

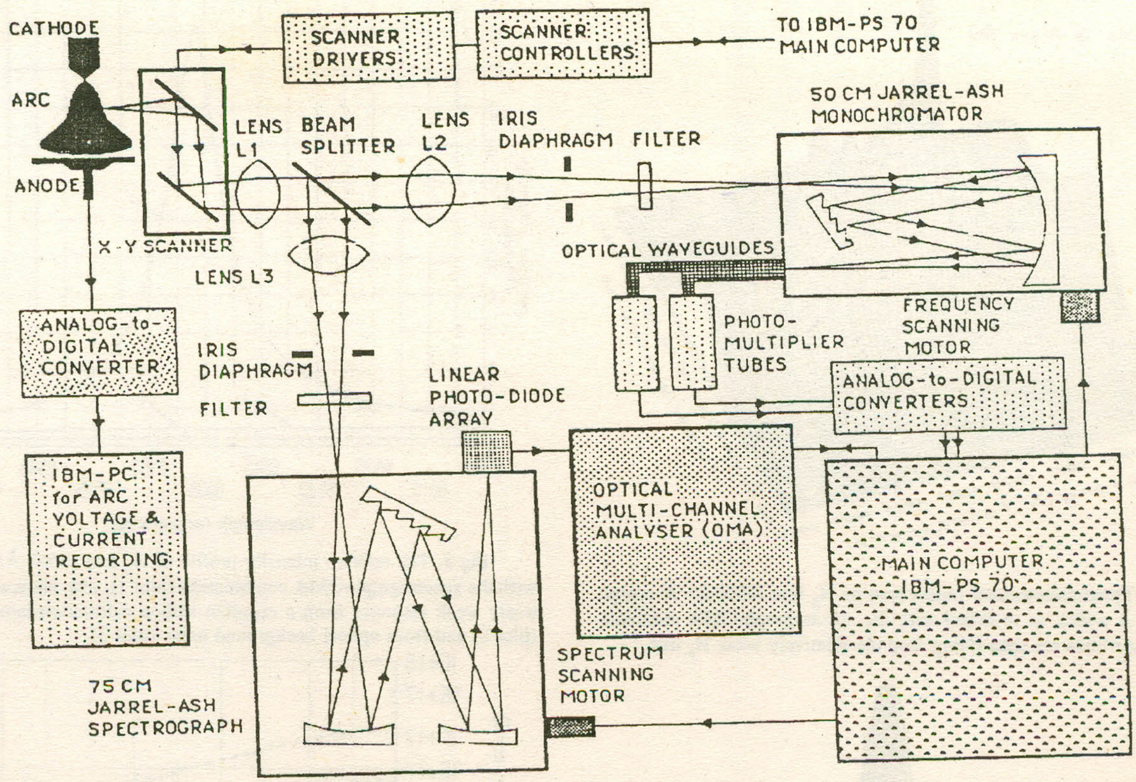

Fig 1. Optical emission spectroscopic set-up employed for the experiment.

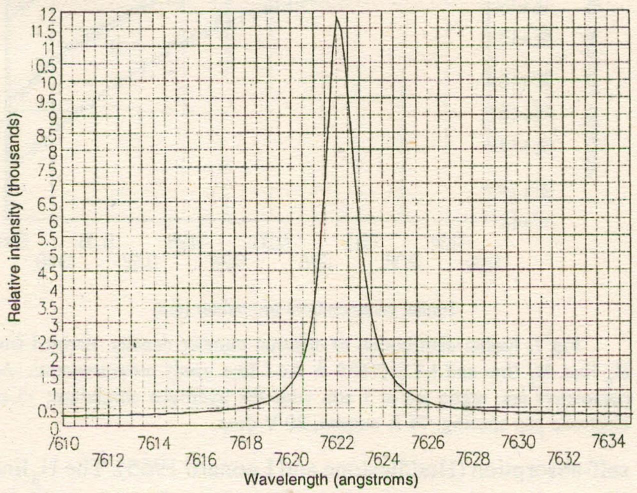

Fig 2. The relative-intensity profile of the strong Ar I line at 7635 Å, as recorded with the emission spectroscopic set up.

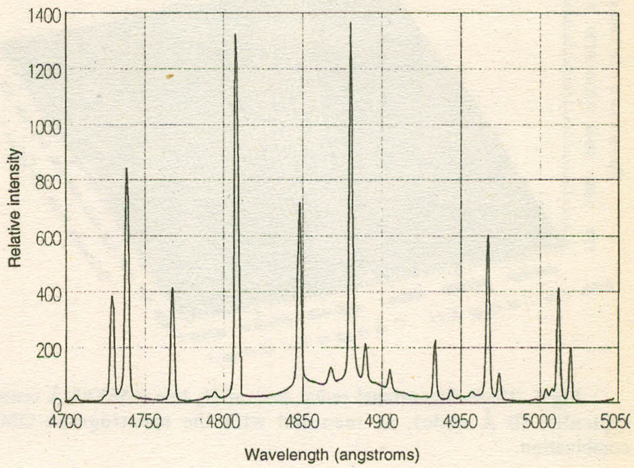

Fig 3. The arc's emission spectrum between 4700 Å and 5050 Å wherein the characteristic hump of the H_β line (centre frequency 4861.33 Å) is discernable between 4825 and 4930 Å.

(plot 1), shows the relative intensity profile of the Stark-broadened H_α line (6563 Å) of hydrogen Balmer series as recorded with the spectrograph-OMA combination; the relative response from a tungsten ribbon calibration-lamp at 2400°K (plot 2) and from optical background (plot 3) are also shown to illustrate the relative strength of the H_α line. Figure 6 shows a three dimensional picture of a radial scan of the strong H_α line (typically 10 Å wide). In contrast to the H_β line, the H_α line does not have any strong argon lines in its vicinity.

Results and Discussion

From the measured half-widths of the Stark-broadened Balmer-lines, electron number densities were computed with the help of the above mentioned equations. In Fig. 7, the

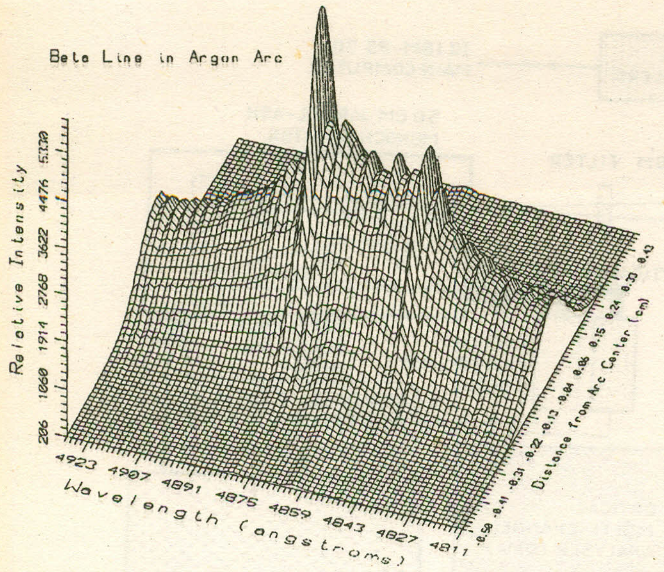

Fig 4. Three-dimensional radial scan of H_β line (4861.33 Å centre, typically 40 Å wide), as recorded with the spectrograph-OMA combination. Strong Ar lines are seen riding atop the relatively weak H_β line.

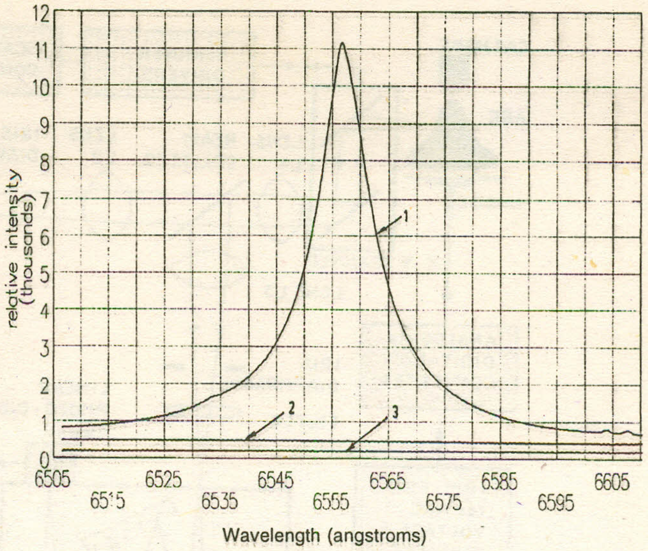

Fig 5. The relative intensity profile of H_α line (6563 Å) as recorded with the spectrograph-OMA combination (plot 1); also shown are the relatively weak response from a tungsten ribbon calibration-lamp at 2400°K (plot 2) and from optical background noise (plot 3).

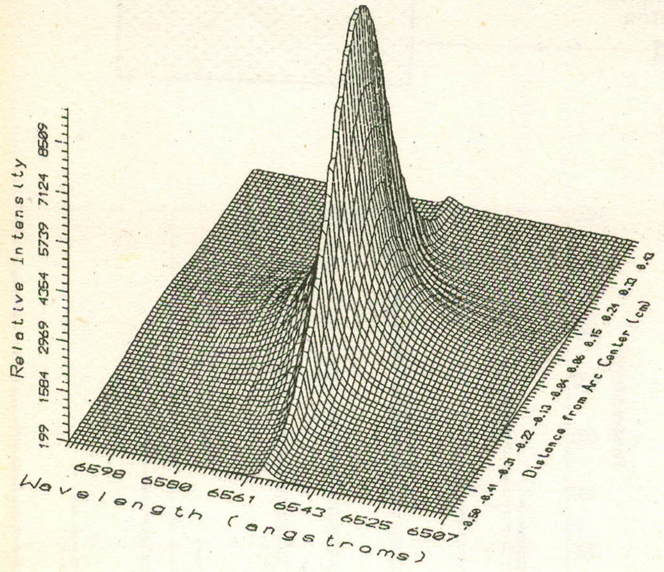

Fig 6. Three-dimensional radial scan of H_α line (6562.85 Å centre, typically 10 Å wide), as recorded with the spectrograph-OMA combination.

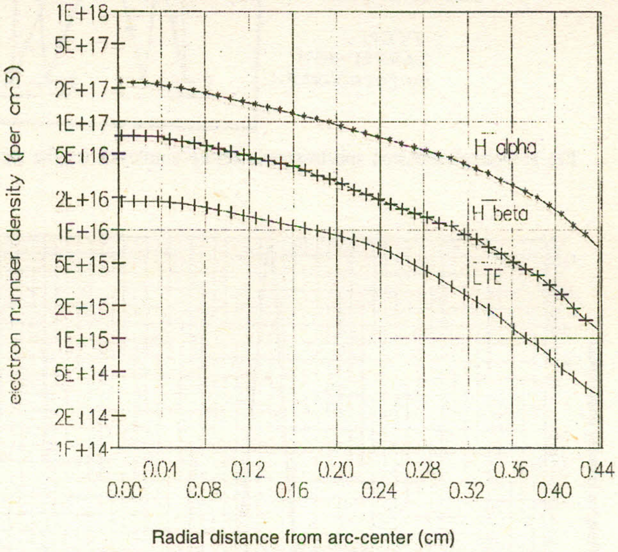

Fig 7. Radial distribution of electron number density, derived from H_α line, H_β line and LTE (7635 Å Ar I line used) measurements. Arc parameters are: argon arc at 1 atm with 1% hydrogen admixture; 13 cm electrode gap spacing; 75 A current; 20 V drop.

resulting electron densities from Stark broadening H_α and H_β lines are compared with LTE calculations by absolute line intensity of 7635 Å Ar I line. The number densities have been plotted as a function of radial distance from the centre of the arc. The H_α line results show an order-of-magnitude higher number densities than those from LTE measurements. The H_α line results are generally known to be inaccurate because its theory has not been brought to the same state of refinement (Huddlestone and Leonard 1965) as that for H_β line and, additionally, the H_α line is known to suffer from significant self-absorption (Huddlestone and Leonard 1965). The H_β line, however, is usually the first choice for Stark-broadening applications, its theory is well developed, and results are expected to be accurate within 10% (Griem 1964). The H_β line results turned out to be about 4 times higher than LTE results. This difference is attributable to two possible reasons: first, the strong Ar I 7635 Å line itself also suffers from self-absorption(Olsen 1963a & b; Bober and Tankin 1969; Hadded and Farmer 1984) and second, there may be a considerable deviation from LTE. Such a strong deviation from LTE is well understood from the following explanation. The investigated arc is at a relatively low current (75 A), temperatures are relatively low (7,000-10,000°K), and consequent electron number densities n_e are also low (10^{16} cm^{-3}). The resulting plasma, though optically transparent, is not collision dominated. Therefore, the inelastic collision rate between electrons and atoms does not exceed that of radiation loss. The number of emission processes exceeds the number of photo-absorption processes on account of the diluted radiation field. Consequently, the excited atomic levels get underpopulated while the ground levels get overpopulated. Thus, the value of line emission coefficient (Eq. 1) is actually less than its expected LTE value and n_e (LTE) is smaller than n_e (Stark broadening).

Conclusion

A fast, accurate and comprehensive emission spectroscopic set-up was employed to study the deviations from LTE in thermal plasmas. The Stark-broadened H_β and H_α hydrogen line profiles were recorded along with the intensity of an Ar I spectral line. The resulting electron number densities from hydrogen lines were compared with those derived from absolute intensity measurements of the 7635 Å Ar I line. The H_α line showed an order-of-magnitude higher number densities than LTE measurements. The H_α results are generally known to be inaccurate because this line is known to be self-absorbing and its refined Stark-broadening parameters have not been calculated. The H_β line is usually the first choice for Stark-broadening calculations; its theory is well developed, and results are expected to be accurate within 10%. Results from the H_β line turned out to be about 4 times higher than LTE results. This difference is attributed to two possible reasons: first, the strong Ar I line itself also suffers from self-absorption; and second, there may be a considerable deviation from LTE.

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