Laser Induced Fluorescence Spectroscopy of Atoms in a Hollow Cathode Discharge Lamp

Agung Bambang Setio Utomo[1)] & Hans Helmut Telle[2)]
[1)]*Dept of Physics, FMIPA, Gadjah Mada University*
[2)]*Dept of Physics, Univ of Wales at Swansea, UK*

ABSTRACT

It has been demonstrated in this work that commercial hollow cathode discharge lamps can be used for Laser Induced Fluorescence technique by sending the laser beam into the cathode discharge lamp. Experiments have been performed using a single mode diode laser to investigate selected lines of argon (~772 nm). After resonant laser excitation on a certain transition, most of the other lines in the spectrum change their intensities in the LIF experiment. The highest intensity increment is observed for the wavelengths which originate from the same excited level ($2p_7$) as the one accessed by the pumping radiation. Further very strong intensity changes are observed for transitions from the excited levels nearest to the pumping level, obviously due to collisional transfer processes.

Keyword: Fluorescence, discharge, argon, diode

INTRODUCTION

The most commonly used tunable lasers still are dye lasers. However, they are rather complex and expensive and rarely have become an alternative to the established methods in routine analysis, replacing classical spectroscopy tools. In contrast, it may be argued that the rapid development of semiconductor diode lasers will have a strong impact on analytical spectroscopy. Step by step these devices will surely replace the dye laser in numerous applications. The objective of the present work was to use a tunable diode laser for laser induced fluorescence spectroscopic technique. In this work a commercial hollow cathode discharge lamp was used to provide analyzing for the diode laser radiation. That lamp was used because they are relatively inexpensive for almost all of the elements of the Periodic Table and their electrical noise is usually low, often at the level of shot noise. While a standard low-power single mode laser diodes were used, they are cheap in cost, have a reasonably narrow linewidth, exhibit low power consumption and are relatively easy to operate.

It has been argued that commercial hollow cathode discharge lamps have limited use in many laser spectroscopic applications because of their geometrical design. However, in this work we have demonstrated that they indeed can be used for laser induced fluorescence spectroscopy in argon transitions.The technique of fluorescence spectroscopy involves the processes of absorption and fluorescence in sequence. The light passing through an atomic or molecular cell is absorbed when in resonance with a certain transition, and the deactivation of atoms or molecules in excited states may usually be via emission of light at the same wavelength.

In the case of resonance fluorescence, the emitted energy is the same as the absorbed energy, while in stepwise line fluorescence the atom is excited to a state above the first excited state. This is followed by deactivation to the first excited state, followed by emission of light at a wavelength different to the excitation wavelength to return to the ground state. Another type is direct line fluorescence. Excitation raises the electron to an excited state above the lowest available state just as in the case of stepwise line fluorescence. The excited electron returns to the ground state by emitting radiation to an intermediate state, followed by a radiationless transition to the ground state. Another fluorescence process known as sensitized fluorescence involves a transfer of excitation energy from one atom to another atom. The energy difference between the excited states of one atom to the excited state of another atom will be absorbed as kinetic energy by atoms of both atoms; again, the fluorescence is at a wavelength different from that of the excitation. (Smyth & Schenck 1978, Smyth *et al.* 1978)

Further processes, involving collisions between excited atoms and electrons, are radiative deexcitation by electron - metastable

atom collisions. Other specific processes contribute to the losses of excited atoms, such as superelastic collisions, in which excitation energy is transferred into kinetic energy to increase the electronic temperature and radiative de-excitation against the cell's walls are also encountered, and they are sometimes required to describe the complete balance of the discharge processes. (Jung & Lee 1999, Mahmood *et al.* 2004, Manzano *et al*. 1994, Piracha *et al.* 2009).

METHODS

The set-up for the laser induced fluorescence (LIF) experiment is shown in figure 1. The diode laser beam was chopped and thereafter sent into the hollow cathode discharge slightly off-axis from the hollow cathode. A fraction of the diode laser beam was reflected by the cathode surface, and this radiation, together with the hollow cathode discharge light, was sent via an optical fibre to the monochromator which is equipped with a CCD diode array detector. To monitor the diode laser beam being in resonance with a certain transition of argon line in the discharge (the 772.3761 nm line of argon), the optogalvanic signal was sent to the DSA. The fluorescence spectrum, recorded by the CCD diode array detector via a monochromator, was acquired by the computer system for later data processing.

These measurements were only performed for one particular transition in argon, namely the 772.3761 nm line while by using the CCD diode array spectrometer as a detector system and the lithium / argon hollow cathode discharge lamp as the sample system, the fluorescence from a number of argon lines was detected in the wavelength range accessible to our diode lasers.

RESULTS AND DISCUSSION

It is well known that the tuning curve of diode lasers exhibits a stair-case form when it is tuned in temperature at a fixed injection current or vice versa. In general, the wavelength tuning is discontinuous and hops of one or several cavity modes are observed. Thus some generalities concerning diode laser tuning curve can be observed; usually each diode laser has a unique tuning curve, and a particular diode laser has a different tuning curve at a different injection current.

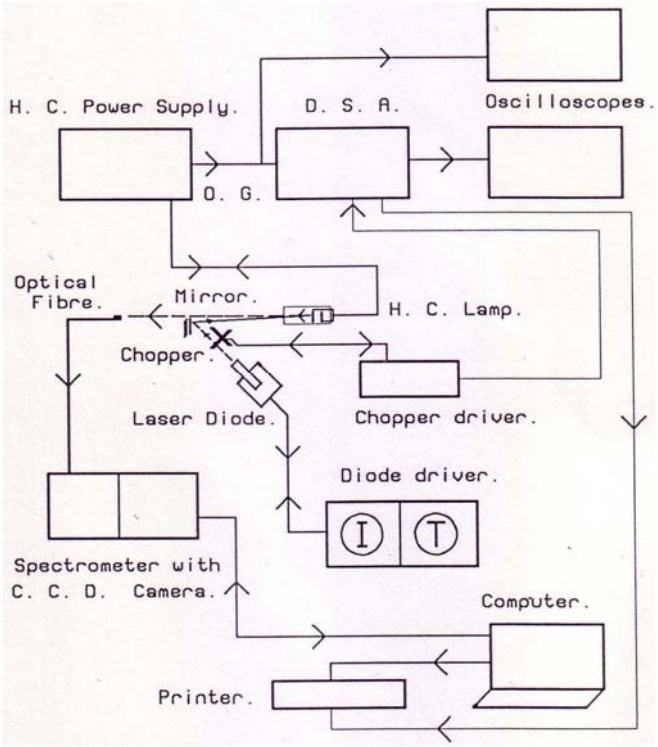

Figure 1. A schematic arrangement for laser induced spectroscopy.

The tuning curve of diode laser (ML 6413 A; λ_p ~ 773 nm) at an injection current of 90 mA is shown in Figure 2; for the measurement our CCD diode array spectrometer was used. The range of temperature tuning is 1.5 - 34°C which roughly covers the wavelength range 772 - 777 nm.

It is a general characteristic of diode lasers, those by judicious choices of temperature and injection current / power, the tuning curve can be moved around. When one is interested in a certain wavelength, with reference to the Figures 2, one can raise or lower the injection current in order to shift a continuous part of the temperature tuning region around the wavelength range of interest. By measuring the laser wavelength as a function of temperature at a certain injection current, it is rather easy to find the laser parameters that yield the desired wavelength. However, it can not be guaranteed that a specific laser will tune to the desired wavelength. For any particular diode laser, there is a possibility that a tuning range has a mode jump at the desired wavelength and it is not always possible to move this mode jump around as much as one would like (Camparo 1985).

Argon which has closed electron shells in its ground state has its four lowest excited levels due to the $3p^5$ 4s configuration. It is interesting to address the two transition of the $3p^5$ 4s - $3p^5$ 4p configuration which have wavelengths of λ = 772.376 nm and 772.421 nm, those two lines, which are separated by less than 0.05 nm (Reader & Corliss, 1992).

The optogalvanic line spectrum for argon at λ = 772.376 nm as shown in Figure 3. The line at λ = 772.376 nm originates from the transition $3p^5$ 4s - $3p^5$ 4p ($\equiv 1s_5 - 2p_7$) and that at λ = 772.421 nm is due to the $3p^5$ 4s - $3p^5$ 4p ($\equiv 1s_3 - 2p_2$) transition. Both lower levels, i.e. $1s_3$ and $1s_5$, are metastable levels (Murnick *et al.* 1989). These two lines were not resolved in the experiments conducted by Nestor (1982) who used an ordinary pulsed dye laser.

Such an emission spectrum, the particular argon lines have wavelengths of λ_1= 763.5106 nm, λ_2= 772.3761nm, λ_3= 772.4207nm, λ_4= 794.8176nm, λ_5= 800.6157nm, λ_6= 801.4786nm, λ_7= 810.3693nm and λ_8= 811.5311 nm; they stem from the transitions of $\lambda_1= 1s_5 - 2p_6$, $\lambda_2= 1s_5 - 2p_7$, $\lambda_3= 1s_3 - 2p_2$, $\lambda_4= 1s_3 - 2p_4$, $\lambda_5= 1s_4 - 2p_6$, $\lambda_6= 1s_5 - 2p_8$, $\lambda_7= 1s_4 - 2p_7$ and $\lambda_8= 1s_5 - 2p_9$, respectively.

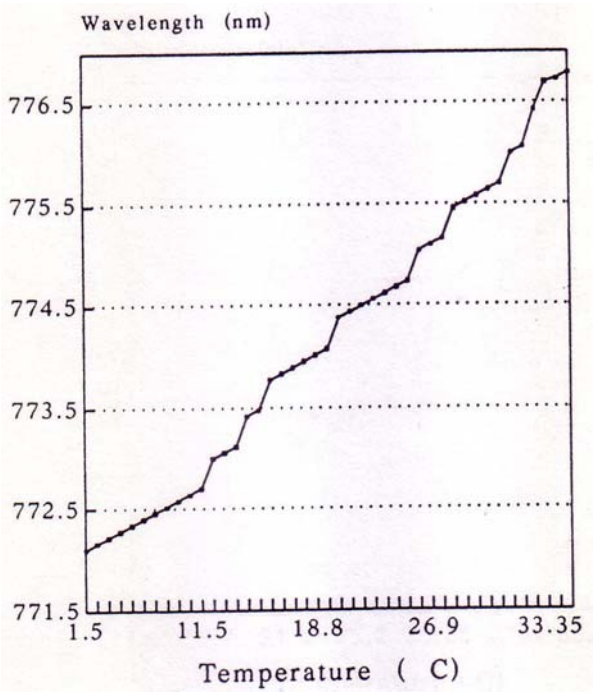

Figure 2. The tuning curve of a diode laser (λ_p ~ 773 nm) at an injection current of 90 mA.

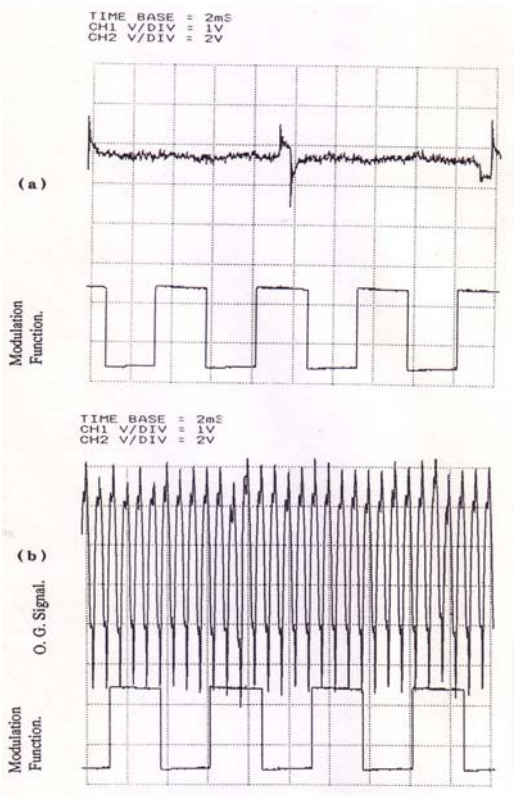

Figure 3. When the laser is off-resonance no OG signal is observed, the noise is shown (trace a); on-resonance the signal OG for a certain transition in argon is much larger than the noise component (trace b) (The laser radiation is chopped at about 200 Hz.).

At off-resonance, the atomic and diode laser system in the hollow cathode is undisturbed (see Figure 4a). Only the line intensity at 772 nm is largely increased due to the reflected light from the diode laser. It should be noted, that the two argon lines and the diode laser light are not resolved by our spectrometer, and only a single peak is observed. When the diode laser was tuned in-resonance with the λ_2= 772.3761 nm line of the $1s_5$ - $2p_7$ argon transition, some of the diode laser light is being absorbed. The spectrum resulting from on-resonance excitation is shown in figure 4b, and clearly a decrement of the diode laser intensity is observed caused by the atomic absorption. The decrease in intensity due to atomic absorption is roughly ~ 50 % which is much larger than that in the "perpendicular" absorption configuration. This is most likely caused by the much longer light path, and therefore more particles are involved in the atomic-light interaction. The light in the sample travels twice in parallel direction to the cylinder axis, forward and backward, while in the ordinary absorption experiment the light travels only once through the sample, perpendicular to the cylinder axis (Setio Utomo & Telle 2009).

After pumping resonantly on a certain transition, the excited state population will decay; some de-excitation may occur directly to lower states by optical transitions, but also transfer of excitation energy to other higher excited states may take place, or non-radiative decay to other lower states may be induced in collisions. As a result, an intensity increase in a number of argon lines is observed after pumping resonantly on the $1s_5$ - $2p_7$ argon transition at λ_2= 772.3761 nm. As a result of the resonant laser excitation, most of the lines in the spectrum change their intensities (Figure 4 or Figure 5). The highest increment is observed for the λ_7 = 810.3693 nm line ($1s_4$ - $2p_7$ transition); this line originates from the same excited level ($2p_7$) as the one accessed by the pumping radiation.

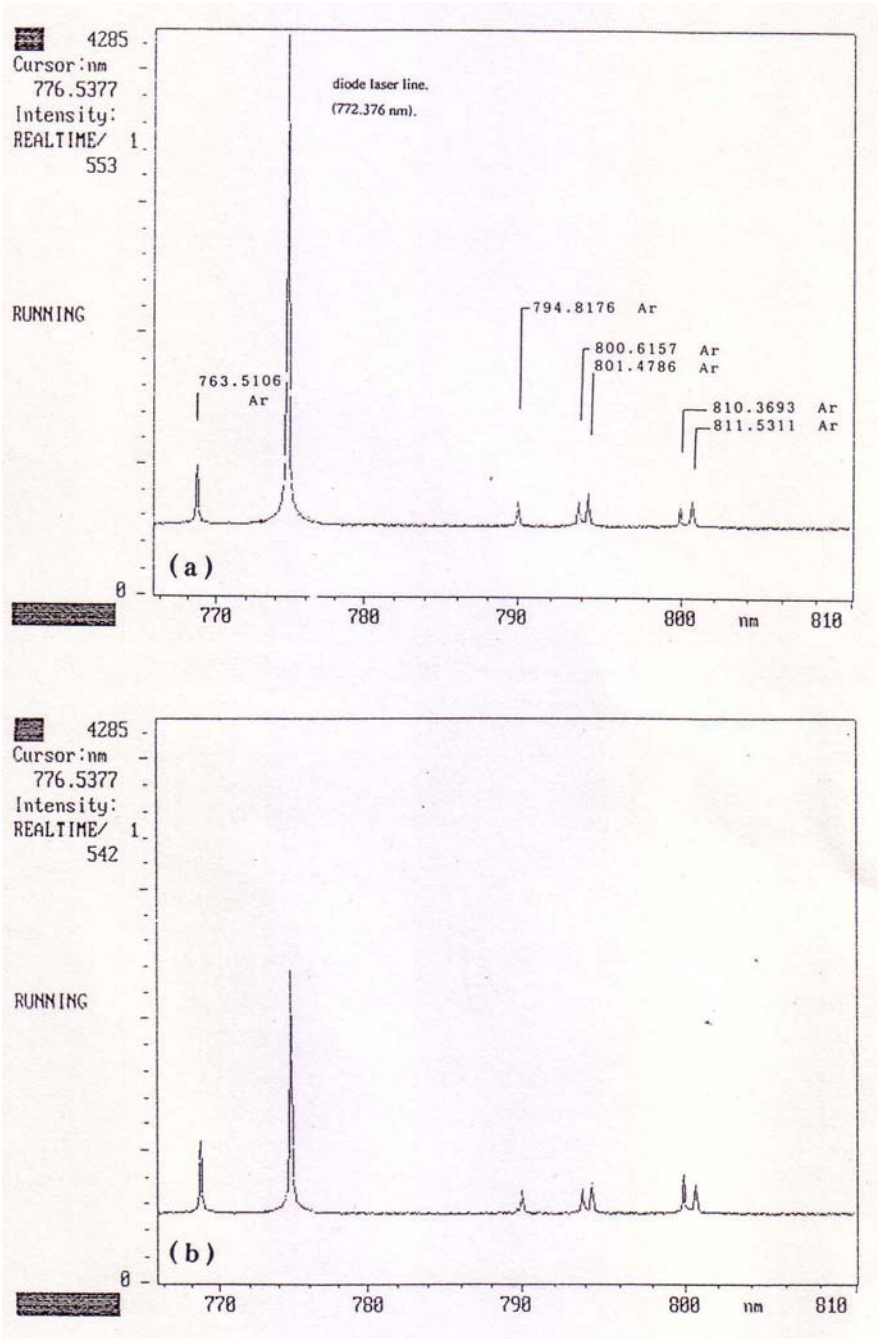

Figure 4. a) diode laser off-resonance, near 772 nm, b) diode laser on-resonance with the 772.376 nm transition in argon

Further very strong intensity changes are observed for transitions from the excited levels nearest to the pumping level ($2p_7$), i.e. from $2p_6$ - $1s_5$ (λ_1= 763.5106 nm) and $2p_8$ - $1s_5$ (λ_6= 801.4786 nm) (compare Figure 5a for off-resonance and Figure 5b for on-resonance). A partial energy level diagram of argon is shown in Figure 6; relevant transitions are indicated where a bold line is the pumping transition, the bold dashed line is a direct fluorescence line, and the dashed lines are those which change intensity significantly.

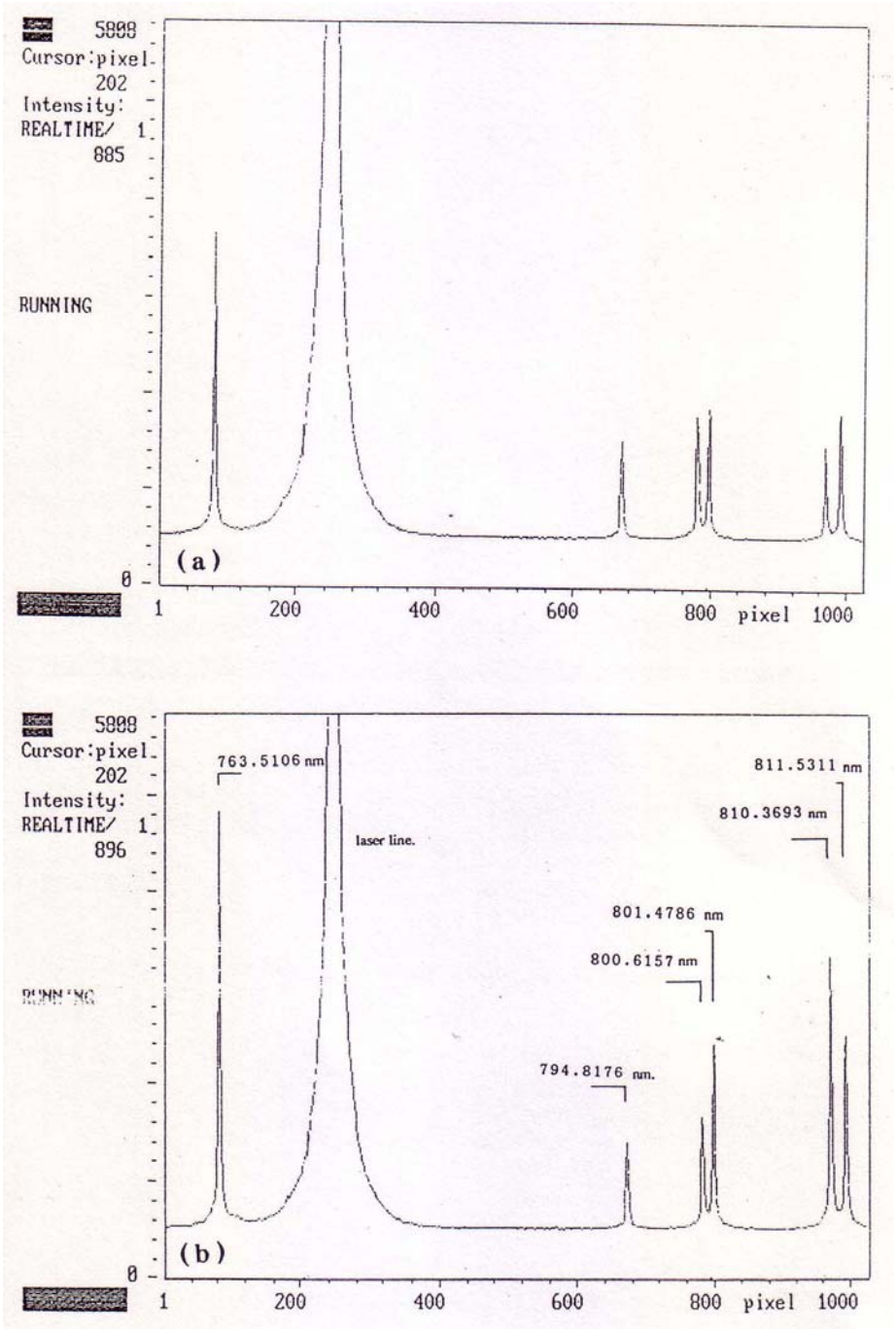

Figure 5. Emission spectrum of argon, same as figure 4a but with expanded intensity scale: a). diode off-resonance, b) diode laser on-resonance.

CONCLUSION

The technique of laser-induced fluorescence is also possible, and was demonstrated for a transition in argon. Besides the direct LIF transitions also collision-induced transitions are observed, and one may deduce information on collisional transfer cross sections.

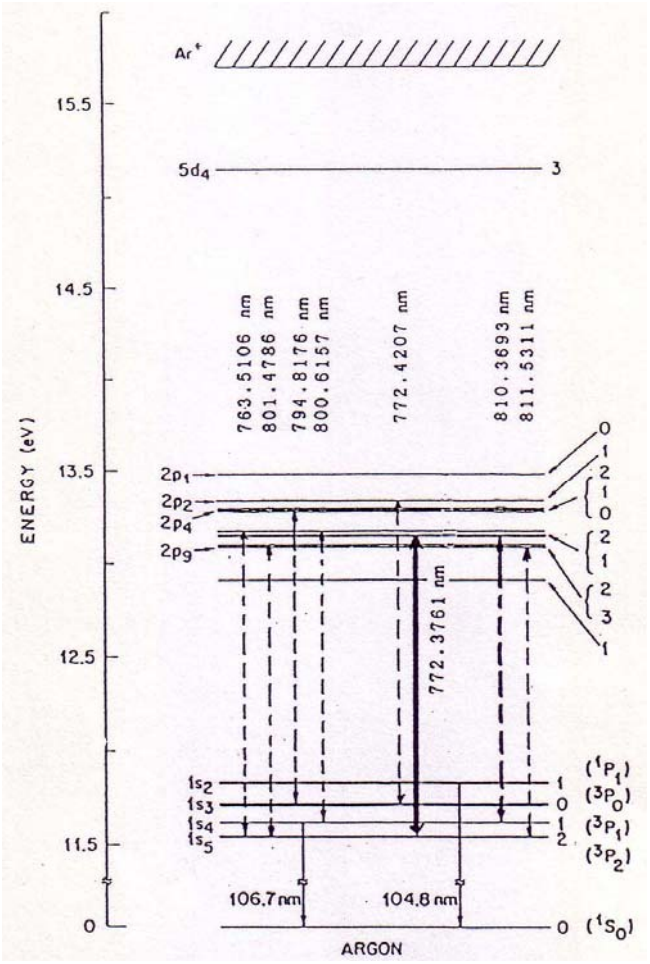

Figure 6. Relevant transitions in argon observed in the Laser Induced Fluorescence experiment. (_____ excitation line; ___ ___ ___ direct fluorescence line and _ _ _ _ _ _ collisionally induced fluorescence)

REFERENCES

Camparo JC. 1985. The Diode Laser in Atomic Physics Cont. *Phys*. **26**: 443.

Jung EC & Lee J. 1999. Specific behaviors of dynamic optogalvanic signals of an argon hollow cathode discharge. *Optics Comm* **161**: 149

Mahmood S, Anwar Ul Haq M, Riaz M, Baig MA. 2004. Temporal evolution and variation of laser optogalvanic signals in the spectra of inert gases. *Optics Comm* **236**: 411.

Manzano FA, Slezak VB, D'Arcurso V. 1994. Simple model for the optogalvanic effect in a neon negative glow discharge. *Optics Comm* **109**: 65.

Murnick DE, Robinson RB, Stoneback D, Colgan MJ, Moscatelli FA. 1989. Optogalvanic Signal from Argon Metastables in a rf Glow Discharge. *App. Phys. Lett.* **54**: 792

Nestor JR. 1982. Optogalvanic spectra of neon and argon in glow discharge lamps. *Appl. Opt.* **21**: 4154.

Piracha NK, Feaver R, Gilani TH, Ahmed R, Ali R, Baig MA. 2009. The study of the 1s 2p optogalvanic transients in a neon discharge plasma. *Optics Comm.* **282**: 2532.

Reader J. & Corliss CH. 1992. N. I. S. T. Spectroscopic properties of atoms and atomic ions database, N. I. S. T. Standard Reference Database 38, Gaithersburg, MD 20809.

Setio Utomo AB & Telle HH. 2009. *A Simple Electronic Device for Optogalvanic and Absorption Spectroscopy of Atoms in A Commercial Hollow Cathode Discharge Lamp in International Conference on Instrumentation, Communications, Information Technology, and Biomedical Engineering*. Proceeding ICICI-BME 2009. ITB Bandung.

Smyth KC & Schenck PK. 1978. Optogalvanic Spectroscopy of a Neon Discharge. *Chem. Phys. Lett.* **55**: 466.

Smyth KC, Keller RA, Crim FF. 1978. Photon Induced Ionization Changes in a Neon Discharge Chem. *Phys. Lett.* **55**: 473.