

Laser Optogalvanic Spectroscopy and Collisional State Dynamics Associated with Hollow Cathode Discharge Plasmas

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Abstract In this chapter we will discuss the laser optogalvanic effect in a discharge plasma environment, specifically associated with an iron-neon (Fe–Ne) hollow cathode lamp. The history of the optogalvanic effect will serve as an introduction to the importance of the phenomena. The theoretical model behind the optogalvanic effect will provide insight into the importance of laser optogalvanic spectroscopy as a tool for spectral characterization of the plasma processes and enhanced understanding of the collisional state dynamics associated with the discharge species in hollow cathode lamps. The present chapter will focus on transition states of neon in the Fe–Ne hollow cathode lamp. The results presented here will use, for illustrative purposes, the waveforms associated with the laser-excited optogalvanic transitions of neon: $1s_4-2p_3$ (607.4 nm), $1s_5-2p_7$ (621.7 nm), $1s_3-2p_5$ (626.6 nm), $1s_5-2p_8$ (633.4 nm) and $1s_5-2p_9$ (640.2 nm). A comparison between the experimentally recorded optogalvanic signal waveforms and the Monte Carlo fitting routine, along with a discussion related to the variation of the (a_i and b_j) fitting coefficients as a function of the discharge current, will illustrate the success of our theoretical model. We will also briefly touch upon the potential applications of the optogalvanic effect at the nanoscale in fields such as graphene-based nanoelectronics and nanoplasmonics.

Keywords Laser optogalvanic spectroscopy • Collisional state dynamics • Hollow cathodes • Iron-neon hollow cathode lamp • Discharge plasmas • Neon • Transitional states • Optogalvanic signal waveforms • Monte Carlo fitting routine • Least-squares analysis • Graphene-based nanoelectronics • Nanoplasmonics

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1 Introduction

Laser optogalvanic spectroscopy is the study of the change in impedance that occurs as a result of irradiating the atoms in a gas discharge environment, such as a hollow cathode, with a laser source; the concomitant variation in impedance is often referred to as the OptoGalvanic Effect (OGE). OGE is a direct consequence of the laser excitation of the atoms/molecules populating the various energy levels of the species present in the discharge plasma, followed by collisions that result in redistribution of the plasma species in energetically favorable states. With advances in laser technology, such as the widespread availability of tunable and short-pulsed lasers, optogalvanic spectroscopy has gained a foothold in the study of plasma species and their atomic/molecular transitions by tuning the laser precisely to specific wavelengths that resonate with the plasma species of interest. In addition, specific collisional state dynamics of a particular species can be investigated because its rate of ionization undergoes changes due to collisions within the discharge plasma. The rate of ionization depends on the probability of atomic ionization occurring after the atom is hit by an electron and also on the duration of the resulting excited state [1], whereby, specifically, an atom has a higher rate of ionization if it is in a metastable state.

At the heart of the laser optogalvanic spectroscopy investigations is a Hollow Cathode Lamp (HCL), which is typically composed of an anode, a cathode and a buffer gas (e.g. neon) encased in a glass enclosure, and is exposed to lasers and other spectral line sources. The use of the HCL allows us to obtain OG signals for the cathode species in addition to the buffer gas. The experiments presented here make use of an Fe–Ne (the notation refers to the composition of the electrode and the buffer gas used) HCL, which allows us to not only determine the OG signals that result from the iron, but also determine the neon transitions at very precise wavelengths. Thus, laser optogalvanic spectroscopy is an ideal tool also for spectral calibration in atomic and molecular spectroscopy.

With the advent of nanotechnology, the study of nanoplasmonics is becoming increasingly important. Laser optogalvanic spectroscopy can play a significant role in understanding the behavior of nanoplasmas [2–4]. In the same fashion that laser optogalvanic spectroscopy has been employed to determine the characteristics of hollow cathode tubes involving metals such as iron and noble gases such as neon [5], this technique has potential applications in the determination of collisional rates and population densities for electrodes made of nanomaterials, such as graphene, which has found extensive use in research involving Li-ion batteries [6–10]. Currently, while research on graphene-based nanoelectronics and nanoplasmas is being carried out, to our knowledge there are no extensive studies using laser optogalvanic spectroscopy and graphene electrodes available in the refereed literature.

2 Literature Review

In this section we will review the advances in the optogalvanic effect and the evolution of the laser optogalvanic spectroscopy research from a historical perspective and delve into more detail into the possible applications of its use in the field of nanoscience.

2.1 The Optogalvanic Effect

The first known publications relating to the optogalvanic effect are seen as early as the 1920s [11, 12]. Foote and Mohler [11] observed ionization of caesium (Cs) vapor occurring when the sample was irradiated with light of wavelength longer than 318 nm, which corresponded to wavelengths at which Cs emits light. The authors deduced that the reason for the ionization was due to the fact that the excited atoms collided with others and caused the ionization of the sample. In 1928, Penning observed this same phenomenon, to which he referred to as a new photoelectric effect [12]. Penning detected a variation in the impedance associated with the discharge of an element when irradiated with the emission of another identical discharge, which later came to be known as the OptoGalvanic Effect (OGE). Other similar effects were observed through a wide variety of experiments during the subsequent decades. In 1930, Terenin [13] observed the OGE in molecules while studying the photoionization of salt vapors. Joshi [14–16] independently discovered the same effect (and referred to it as the Joshi Effect), while studying chlorine in a discharge tube, and noted that the current through the discharge would change when the sample was irradiated with energies equal to the difference in energy between the ground and excited states. However, some scientists argued that the Joshi Effect was different from the Optogalvanic Effect on the grounds that one referred to a voltage rise and the other to a current rise [17]. Kenty [18] and Meissner and Miller [19] studied the effect in mercury (Hg) and helium (He) discharges, respectively. In the 1960s, Garscadden et al. [20] also observed the OGE when a change in the discharge current manifested itself as moving striations in a He–Ne discharge.

While the OGE was observed through multiple experiments over half a century, it was not until the development of the tunable dye laser that such investigations took center-stage and became mainstream. Green et al. [21] showed that high-sensitivity spectra could be obtained using tunable lasers using galvanic detection of optical absorptions in a gas discharge [21] and also via detection of species in flames [22]. Green et al. measured a change in the voltage across the discharge tube while irradiating the sample at a laser wavelength corresponding to a transition of the sample under investigation. The authors determined that such a change in voltage could be used as a way to characterize materials in the discharge without the use of an optical detection device, unlike techniques such as fluorescence. This type of research approach also illustrated the usefulness and applications of using a

hollow cathode lamp as the gas discharge environment, which allowed not only excited state transitions but resonance transitions as well to be observed. A year later, in 1977, King et al. [23] showed how direct calibration of laser wavelength and bandwidth using the OG signal provided a simple and yet highly accurate calibration tool for tunable dye lasers. Due to the continued rapid development of tunable dye lasers and Green's pioneering research, laser optogalvanic spectroscopy became a widespread spectroscopic technique used in the study of atoms and molecules in a discharge environment, especially as it relates to their ionization, transition states and collisional dynamics in response to laser excitation.

2.2 Optogalvanic Spectroscopy Techniques

In 1979, Lawler et al. [24] reported Doppler-Free Intermodulated Optogalvanic Spectroscopy, a single-photon spectroscopy technique similar to intermodulated fluorescence spectroscopy that utilizes the detection of the impedance change in gaseous discharges. The primary concept of Doppler-free spectroscopy revolved around the circumvention of the Doppler Effect in spectral data. The Doppler Effect in spectroscopy refers to the fact that, if an atom is moving towards a laser source at a certain velocity v then the laser frequency will be upshifted relative to the motion of the atom. Unlike typical optogalvanic techniques at the time, which were Doppler-limited, the laser beam was split into two equal parts, but with different frequencies, which were then sent through the discharge in opposite directions. Due to the fact that the split laser beams propagate in dissimilar directions, they interact with different velocity groups, those with equal but opposite velocities. However, when the laser frequency matches the atomic/molecular absorption frequency, the two laser beams interact with the same atoms/molecules, and in this case with the ones with zero velocity in the direction of the absorption, resulting in a Doppler-free spectrum. Lawler et al. [24] used this technique to study the ^3He transitions $2^3\text{P}-3^3\text{D}$ and found that this technique compared favorably with other Doppler-free techniques of the time, such as High-Resolution Saturation Spectroscopy [25], Saturated-Interference Spectroscopy [26] and Doppler-Free Laser Polarization Spectroscopy [27]. The Optogalvanic Double-Resonance Spectroscopy [28] technique utilized the same concepts as Doppler-Free Intermodulated Optogalvanic Spectroscopy [24]. In this case, the first laser would be tuned to a specific wavelength that would cause precise transitions between upper and lower energy levels, whereas the second laser would excite the molecules in the levels excited by the first laser. Such a twin laser approach resulted in increased sensitivity over other double resonance techniques that did not utilize the concept of optogalvanic spectroscopy.

Two-photon techniques serve as one of the standard tools for exciting atoms to states that are not possible by using single-photon processes. Goldsmith et al. [29] used a continuous wave (CW) dye laser in a He-Ne discharge to observe transitions in ^{20}Ne using Doppler-Free Two-Photon Optogalvanic Spectroscopy. The use of two-photon optogalvanic spectroscopy allowed the study of non-metastable

transitions in addition to metastable and ground state transitions. As a result, a ground-breaking study by Shawlow et al. [29] reported the first optogalvanic spectroscopy observations of non-metastable state transitions of atoms/molecules in a discharge [29].

2.3 Optogalvanic Spectroscopy Studies in a Hollow Cathode Lamp Discharge

Misra et al. [30] reported a comprehensive list of over 350 optogalvanic transitions in the 337–598 nm region using a pulsed tunable dye laser and an iron-neon (Fe–Ne) hollow cathode discharge. In conjunction with simultaneously recorded interference fringes, a subset (223) of these OG transitions arising from neon permitted the calibration of dye laser frequencies in the visible and near ultraviolet to 0.3 cm^{-1} accuracy. The authors also reported in the same paper [30] that the waveform shapes of the distinct OG transitions of neon at wavelengths (in air) 3510.721, 3515.190, and 3520.471 Å, respectively, recorded with a steady discharge current of 0.5 mA and a laser pulse energy of 20 μJ , were quite different. The same authors investigated the polarity of OG transitions of neon further [31] by focusing on a total of twenty nine OG transitions in the near UV and visible that could be explained in terms of processes that affect the population of neon atoms in metastable states. A close inspection of the oscilloscope traces showed conclusively that the OG signals arising from metastable neon energy levels exhibit waveforms that are negative in character (corresponding to increased ionization current) and subsequently became positive (due to decreased ionization current). In contrast, the OG signals arising from transient non-metastable levels were either completely negative or inverted in shape as compared to those from longer-lived metastable levels. More recently, experimental investigations and mathematical modeling of the OG waveforms of laser-excited Fe–Ne hollow cathode lamp transitions have been carried out in great detail jointly by Han and Misra [5, 32, 33]. A mathematical rate equation model has been developed that incorporates the various processes contributing to the generation of the OG signal waveforms in a laser-stimulated hollow cathode discharge plasma. The experimentally observed waveform was fitted employing a nonlinear least-squares Monte Carlo technique to determine the pertinent amplitude coefficients, decay rates, and the instrumental time constant, in order to better characterize the collisional processes taking place in a hollow cathode discharge plasma.

2.4 Applications Involving Nanomaterials and Nanoplasmas

As mentioned in the introduction, laser optogalvanic spectroscopy has potential prospects in applications utilizing nanomaterials and nanoplasmas. In particular, the development of graphene-based electrodes for use in hollow cathode lamps holds

promise for intriguing discharge plasma experiments using laser optogalvanic spectroscopy. Additionally, investigations of nanoplasmas, plasmas with a lifetime of the order of femtoseconds [2–4], holds potential for ultrashort timescale optogalvanic studies that will shed light on fast processes occurring in discharge plasmas that hitherto have escaped detection and study.

3 Theoretical Model

The laser-induced optogalvanic effect in a discharge environment, such as a hollow cathode lamp, can be summarized in the sequence of events shown in Fig. 1.

First, the relevant energy levels of the atom (e.g. neon) can be identified as follows: the ground energy level (not shown in Fig. 1), a group of relatively closely-spaced energy levels (two are shown and labeled $|1\rangle$ and $|2\rangle$ in Fig. 1, which will be referred to as the “first group”), and another group of relatively closely spaced energy levels above the first group (two are shown and are labelled as $|U_1\rangle$ and $|U_2\rangle$ in Fig. 1, which will be called the “second group”).

Collisions with the electrons in the discharge current excite a large number of atoms into the first group of energy levels, but relatively few of these are excited into the second group. Some of the energy levels in the first group are metastable states, which causes the population in these states to be large. Even if an energy level is not a metastable state and can radiatively decay down to the ground state, radiation trapping by the ground state can significantly lengthen its effective lifetime. The electron collisional ionizations from the first group of energy levels, in turn, contribute electrons to the discharge current. If the atomic population in the first group of energy levels is altered, then the contribution to the total number of free electrons will change due to the different ionization rates of each energy level, resulting in changes in the discharge current.

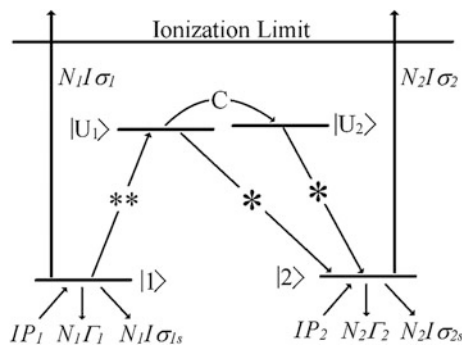


Fig. 1 An energy-level schematic illustrating the collisional dynamics and population distribution giving rise to the Optogalvanic Effect in a Hollow Cathode discharge plasma

A pulsed laser can be used to alter the atomic population in the first group of energy levels. First, a laser can be tuned between $|1\rangle$ and $|U_1\rangle$, exciting the atom from $|1\rangle$ to $|U_1\rangle$. Subsequently, the atom can radiatively decay down to $|2\rangle$ in the first group of energy levels. Alternatively, a collision may transfer the atom from $|U_1\rangle$ to $|U_2\rangle$ and then radiatively decay down to $|2\rangle$. In the end, the net effect of the laser pulse is to transfer some atoms from $|1\rangle$ to $|2\rangle$. This process happens very quickly, on the order of tens of nanoseconds (lifetime of the second group of energy levels). On the time scale of the optogalvanic effect, this transfer may be said to occur instantaneously.

The different population distributions will result in a dissimilar ionization rate, which in turn causes a change in the discharge current. Specifically, the contribution to the discharge current from $|1\rangle$ is reduced because some of the atoms in that energy level are transferred to other energy levels ($|2\rangle$ in the above discussion), while contributions from other energy levels on the receiving end of the population transfer (such as $|2\rangle$) will increase. As a result, the discharge current will undergo a modification, which in turn is captured in the varying OG waveform.

Finally, the ensuing collisions will eventually fill back the population hole in $|1\rangle$ and return its population back to its steady-state value; and this in turn will also occur for the populations in the other energy levels. As a result, the discharge current in the hollow cathode lamp will eventually return to its steady-state value as well.

In order to describe the evolution of the atomic populations in $|1\rangle$ and $|2\rangle$, following the population transfer mentioned above, we write down the following differential equation:

$$\frac{dN_i}{dt} = IP_i - N_i(\Gamma_i + I\sigma_i + I\sigma_{is}) \quad i = 1, 2 \quad (1)$$

where P_i is related to the electron collisional excitation probability from the ground state (not shown in the figure) to $|i\rangle$, in this case, $|1\rangle$ or $|2\rangle$, I is the discharge current, N_i is the atomic population for state $|i\rangle$, Γ_i is the effective spontaneous decay rate for state $|i\rangle$, σ_i is related to the electron collisional ionization probability of state $|i\rangle$, and σ_{is} is related to the electron collisional de-excitation probability of state $|i\rangle$.

Prior to laser excitation, by setting $\frac{dN_i}{dt} = 0$, we obtain the steady-state populations n_i for state $|i\rangle$:

$$n_i = \frac{IP_i}{\Gamma_i + I\sigma_i + I\sigma_{is}} \quad i = 1, 2 \quad (2)$$

To solve Eq. (1), we assume that the ground state holds the vast majority of the atoms so that its population can be treated as constant. As a consequence, we can

treat P_i as constant. Taking into account that Eq. (2) gives the populations for $t = \infty$, we obtain the solutions for Eq. (1):

$$N_i(t) = n_i + c_i \exp[-(\Gamma_i + I\sigma_i + I\sigma_{is})t] \quad i = 1, 2 \quad (3)$$

where $\{c_i\}$ are constants determined by initial conditions due to the pulsed laser excitation to $|U_1\rangle$ and the quick relaxation down to $|2\rangle$. The population changes caused by the laser excitation are:

$$\Delta N_i(t) = N_i(t) - n_i = c_i \exp[-(\Gamma_i + I\sigma_i + I\sigma_{is})t] \quad i = 1, 2 \quad (4)$$

After laser excitation, the atomic population in $|1\rangle$ and $|2\rangle$ can be written as

$$\Delta N_1(0) = -\Delta N_0 \text{ and } \Delta N_2(0) = +\Delta N_0. \quad (5)$$

Inserting the two equations Eq. (5) into Eq. (4) and writing the two equations separately, we obtain:

$$\Delta N_1(t) = -\Delta N_0 \exp[-(\Gamma_1 + I\sigma_1 + I\sigma_{1s})t] \quad (4a)$$

$$\Delta N_2(t) = +\Delta N_0 \exp[-(\Gamma_2 + I\sigma_2 + I\sigma_{2s})t] \quad (4b)$$

Therefore, the Optogalvanic (OG) signal due to ionizations from $|1\rangle$ and $|2\rangle$ is

$$\begin{aligned} S(t) &= \Delta N_1 I \sigma_1 + \Delta N_2 I \sigma_2 \\ &= \Delta N_0 \{-I\sigma_1 \exp[-(\Gamma_1 + I\sigma_1 + I\sigma_{1s})t] + I\sigma_2 \exp[-(\Gamma_2 + I\sigma_2 + I\sigma_{2s})t]\} \end{aligned} \quad (6)$$

Normalizing it to ΔN_0 , we obtain the experimental time-resolved OG signal as

$$s(t) = \frac{S(t)}{\Delta N_0} = a_1 e^{-b_1 t} + a_2 e^{-b_2 t} \quad (7)$$

where

$$a_1 = -I\sigma_1 \quad (8)$$

$$b_1 = \Gamma_1 + I(\sigma_1 + \sigma_{1s}) \quad (9)$$

$$a_2 = I\sigma_2 \quad (10)$$

$$b_2 = \Gamma_2 + I(\sigma_2 + \sigma_{2s}) \quad (11)$$

3.1 The Effect of Plasma/Instrument Relaxation Time on the OG Signal

Neither the discharge plasma nor the detection instrument can respond to changes instantaneously. Let us assume the relaxation time constant to be τ . The actual OG signal observed in an experiment is a convolution of Eq. (7) with a time constant τ :

$$s(t) = \frac{a_1}{1 - b_1\tau} \left(e^{-b_1 t} - e^{-t/\tau} \right) + \frac{a_2}{1 - b_2\tau} \left(e^{-b_2 t} - e^{-t/\tau} \right) \quad (12)$$

We want to point out that since the relaxation time constant τ depends on the discharge conditions, it is not a constant if the discharge current changes.

3.2 Physical Significance of Fitting Coefficients

As seen from Eqs. (8) and (9), the a_1 term in Eq. (12) is negative and the a_2 term is positive. This is because the effect of the pulsed laser is to transfer some population from $|1\rangle$ to $|2\rangle$, resulting in a drop in the contribution to the total ionization from $|1\rangle$, and hence a negative OG signal results due to energy level $|1\rangle$; whereas the reverse holds true for the positive OG signal from energy level $|2\rangle$.

If the first group of energy levels consists of more than 2 individual energy levels, then the OG signal will be an extension of Eq. (12):

$$s(t) = \sum_{i=1}^n \frac{a_i}{1 - b_i\tau} \left(e^{-b_i t} - e^{-t/\tau} \right) \quad (13)$$

where n is the total number of energy levels in the first group. One term in the summation has negative amplitude, which corresponds to the contribution from the initial energy level $|1\rangle$ from which atomic population is transferred to other energy levels initiated by the laser pulse, and the rest of the terms are positive because their corresponding energy levels are on the receiving end of the population transfer.

4 Experimental Set-up for Laser Optogalvanic Spectroscopy

The experimental set-up used is shown in Fig. 2 [5]. A pulsed laser is tuned to each of the studied neon transitions (607.4, 621.7, 626.6, 633.4, and 640.2 nm) and directed to enter an iron-neon (Fe-Ne) Hollow Cathode Lamp (HCL). The discharge current in the HCL is limited by the RC circuit and the current is adjusted to

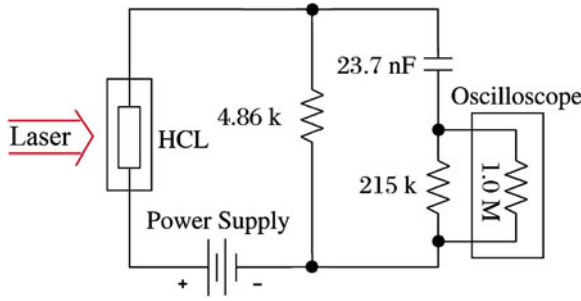


Fig. 2 Schematic experimental arrangement for laser optogalvanic spectroscopy using a Hollow Cathode Lamp (HCL)

be between 2–19 mA via the power supply voltage. A Tektronix TSD 224 digital oscilloscope displays and stores the OG signal. Subsequently, the OG signal waveforms from the oscilloscope are used in the Monte Carlo fitting routine [5].

5 Neon Transitions

Unlike other noble gases, neon can discharge at low currents, such as those used in the present investigation, making it an ideal gas for the study of discharge plasma environments in a hollow cathode lamp. For the neon $1s$ – $2p$ transitions, there are four $1s$ states and ten $2p$ states, which yields a total of 30 radiative transitions [32]. Figure 3 shows these transitions with their corresponding wavelengths in nanometers. Laser optogalvanic spectroscopy, along with the above mathematical formulation, makes it possible to determine the population density distribution in the discharge. We will illustrate the theoretical model by applying it specifically to the following OG transitions of neon in the visible: $1s_4$ – $2p_3$ (607.4 nm), $1s_5$ – $2p_7$ (621.7 nm), $1s_3$ – $2p_5$ (626.6 nm), $1s_5$ – $2p_8$ (633.4 nm) and $1s_5$ – $2p_9$ (640.2 nm). As seen on the arrow connections in Fig. 3, the main idea is that when neon atoms are excited from their original state, $1s_5$ for example, to a state such as $2p_7$, they can subsequently relax back from $2p_7$ to $1s_2$, $1s_3$, $1s_4$ and $1s_5$. Table 1 below summarizes the possible relaxation states for the investigated OG transitions.

5.1 $1s_4$ – $2p_3$ Transition (607.4 Nm)

This particular transition for atomic neon occurs at 607.4 nm, where the neon atoms after excitation can relax down to another state; additionally, it can also relax back to where it started, the $1s_4$ state. The Monte Carlo approach cited above is used to fit the theoretical Eq. (13) to the observed waveform recorded at 607.4 nm. A fuller discussion regarding the fitting process is given below in the Results and Discussion section. The fitted values for the $1s_4$ – $2p_3$ waveform are summarized in Table 2.

Fig. 3 Neon atom transitions between $1s_i$ - $2p_j$ states with corresponding wavelengths (nm) (adapted from Ref. [32] with permission)

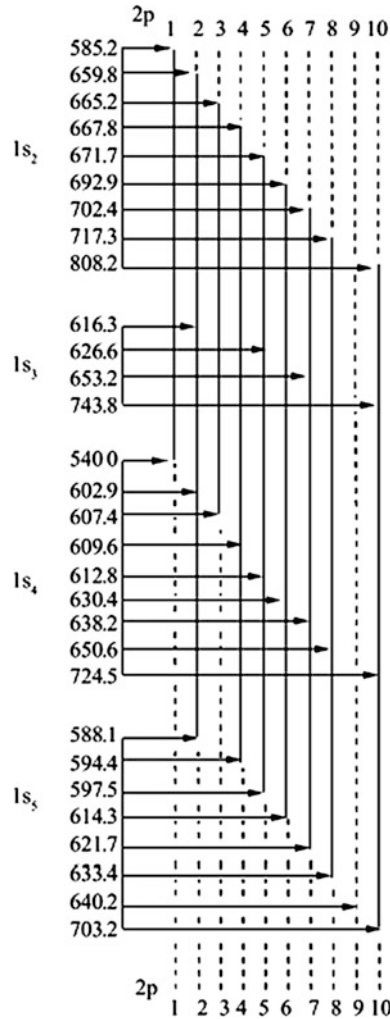


Table 1 Investigated OG transitions of neon and associated relaxation states

Transition	Wavelength (nm)	Relaxation states
$1s_4 \rightarrow 2p_3$	607.4	$1s_2 \mid 1s_4$
$1s_5 \rightarrow 2p_7$	621.7	$1s_2 \mid 1s_3 \mid 1s_4 \mid 1s_5$
$1s_3 \rightarrow 2p_5$	626.6	$1s_2 \mid 1s_3 \mid 1s_4 \mid 1s_5$
$1s_5 \rightarrow 2p_8$	633.4	$1s_2 \mid 1s_4 \mid 1s_5$
$1s_5 \rightarrow 2p_9$	640.2	$1s_5 \mid 2p_j \rightarrow 1s_i$

Table 2 Fitted decay rates obtained from a non-linear least-squares fit of the observed OG waveforms for neon at 607.4 nm for 2–19 mA currents. The fitted a-coefficients are in arbitrary units, while the b-coefficients are in units of $(\mu\text{s})^{-1}$

I (mA)	a ₁	b ₁	a ₂	b ₂	a ₃	b ₃
2	18.258	0.349	−14.491	0.252	0.182	0.005
3	17.672	0.255	−16.919	0.159	3.011	0.075
4	15.130	0.229	−15.984	0.129	4.516	0.074
5	18.754	0.165	−19.918	0.113	3.961	0.061
6	19.813	0.134	−19.922	0.105	2.128	0.050
7	3.280	0.270	−1.345	0.089	–	–
8	2.114	0.672	−0.87164	0.103213	3.165	0.137
9	2.047	0.642	−3.34231	0.100771	3.540	0.124
10	1.950	0.613	−3.67748	0.102807	3.834	0.121
11	1.687	0.704	−5.05266	0.116876	5.427	0.135
12	1.452	0.944	−2.08021	0.120003	2.687	0.171
13	1.316	1.065	−2.06138	0.127232	2.739	0.181
14	1.261	1.172	−2.58873	0.136241	3.341	0.184
15	1.251	1.416	−2.32504	0.142215	3.158	0.198
16	1.194	1.441	−2.40965	0.144766	3.272	0.201
17	1.153	1.452	−3.08785	0.150483	3.913	0.195
18	1.223	1.450	−3.24175	0.148668	4.054	0.192
19	1.165	1.517	−3.62614	0.158177	4.498	0.199

5.2 $1s_5$ – $2p_7$ Transition (621.7 Nm)

The $1s_5$ – $2p_7$ transition is observed around 621.7 nm, where the neon atoms after excitation can relax down to three additional states, namely $1s_2$, $1s_3$, and $1s_4$, plus of course the original $1s_5$ state. The fitted values for the $1s_5$ – $2p_7$ waveform are given in Table 3.

5.3 $1s_3$ – $2p_5$ Transition (626.6 Nm)

This particular transition at exists around 626.6 nm, where the neon atoms after excitation can relax back to three state, namely the $1s_2$, $1s_4$ and $1s_5$ in addition to relaxing back to $1s_3$. According to the work put forward, the observed waveform can be fitted to the expression in Eq. (13). The values fitted are given in Table 4.

Table 3 Fitted decay rates obtained from a non-linear least-squares fit of the observed OG waveforms for neon at 621.7 nm for 2–19 mA currents. The fitted a-coefficients are in arbitrary units, while the b-coefficients are in units of $(\mu\text{s})^{-1}$

I (mA)	a ₁	b ₁	a ₂	b ₂
2	1.467	0.164	−0.625	0.019
3	2.202	0.144	−1.167	0.031
4	3.419	0.105	−2.366	0.040
5	8.575	0.054	−7.866	0.041
6	2.875	0.028	−2.564	0.016
7	0.758	0.107	−0.453	0.011
8	0.776	0.200	−0.411	0.038
9	1.298	0.145	−0.978	0.070
10	1.551	0.147	−1.230	0.082
11	1.698	0.150	−1.381	0.090
12	1.868	0.153	−1.554	0.097
13	1.956	0.157	−1.641	0.103
14	1.951	0.163	−1.632	0.107
15	1.862	0.170	−1.535	0.109
16	1.780	0.176	−1.445	0.110
17	1.799	0.179	−1.457	0.112
18	1.750	0.187	−1.402	0.116
19	1.781	0.190	−1.433	0.120

Table 4 Fitted decay rates obtained from a non-linear least-squares fit of the observed OG waveforms for neon at 626.6 nm for 2–19 mA currents. The fitted a-coefficients are in arbitrary units, while the b-coefficients are in units of $(\mu\text{s})^{-1}$

I (mA)	a ₁	b ₁	a ₂	b ₂
2	14.037	0.237	−4.392	0.034
3	14.195	0.180	−6.314	0.041
4	27.220	0.092	−21.431	0.056
5	20.285	0.069	−16.302	0.041
6	4.849	0.093	−2.320	0.009
7	4.935	0.454	−0.993	0.006
8	5.131	0.353	−1.906	0.036
9	5.368	0.323	−2.402	0.051
10	5.290	0.335	−2.426	0.056
11	5.165	0.356	−2.361	0.059
12	5.914	0.306	−3.218	0.088
13	5.859	0.314	−3.232	0.093
14	5.773	0.324	−3.188	0.098
15	5.764	0.332	−3.167	0.101
16	5.827	0.336	−3.191	0.105
17	5.909	0.343	−3.159	0.105
18	5.765	0.354	−3.036	0.106
19	5.711	0.360	−3.019	0.110

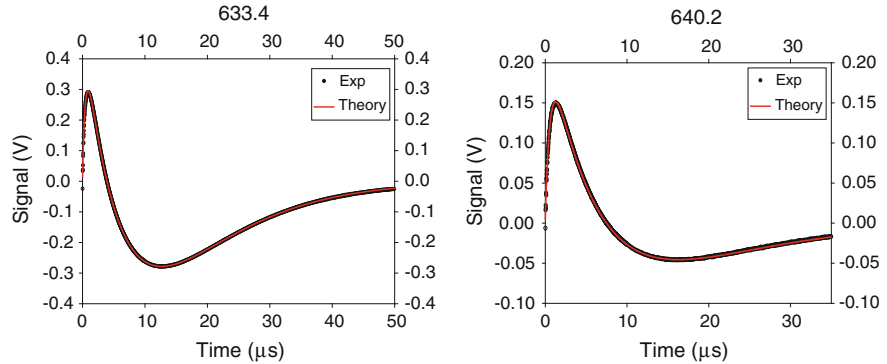


Fig. 4 Time variation of the OG signal at 2.0 mA fitted to the mathematical model for the OG waveforms at 633.4 and 640.2 nm illustrating the similarity between experimental and theoretical fits for each neon transition studied

5.4 $1s_5-2p_8$ Transition (633.4 Nm)

This particular OG transition is recorded around 633.4 nm, where the neon atoms after excitation can relax to three states, namely $1s_2$, $1s_4$, and $1s_5$. The observed waveform can then be fitted to the expression in Eq. (13). The fitted coefficients for the $1s_5-2p_8$ waveform (shown in Fig. 4) are summarized in Table 5.

Table 5 Fitted decay rates obtained from a non-linear least-squares fit of the observed OG waveforms for neon at 633.4 nm for 2–19 mA currents. The fitted a-coefficients are in arbitrary units, while the b-coefficients are in units of $(\mu s)^{-1}$

I (mA)	a_1	b_1	a_2	b_2
2	2.983	0.169	-1.317	0.028
3	14.192	0.179	-6.330	0.041
4	30.874	0.089	-25.157	0.057
5	22.296	0.068	-18.324	0.042
6	4.854	0.092	-2.334	0.009
7	5.004	0.464	-0.989	0.006
8	5.132	0.352	-1.915	0.036
9	5.375	0.322	-2.408	0.052
10	3.221	0.137	-2.776	0.094
11	3.221	0.144	-2.774	0.099
12	3.096	0.152	-2.642	0.103
13	2.999	0.159	-2.520	0.105
14	3.080	0.165	-2.591	0.111
15	2.852	0.172	-2.356	0.113
16	3.221	0.173	-2.720	0.120
17	3.571	0.176	-3.070	0.128
18	2.130	0.205	-1.622	0.117
19	2.153	0.210	-1.644	0.121

Table 6 Fitted decay rates obtained from a non-linear least-squares fit of the observed OG waveforms for neon at 640.2 nm for 2–19 mA currents. The fitted a-coefficients are in arbitrary units, while the b-coefficients are in units of $(\mu\text{s})^{-1}$

I (mA)	a ₁	b ₁	a ₂	b ₂
2	4.113	0.068	−3.875	0.059
3	4.280	0.069	−4.036	0.061
4	4.384	0.064	−4.134	0.055
5	9.890	0.063	−7.829	0.033
6	1.035	0.017	−0.957	0.010
7	0.289	0.168	−0.114	0.033
8	0.554	0.131	−0.371	0.073
9	0.945	0.126	−0.746	0.092
10	1.007	0.132	−0.792	0.097
11	0.616	0.156	−0.382	0.087
12	0.772	0.153	−0.522	0.097
13	0.789	0.159	−0.522	0.101
14	1.018	0.156	−0.736	0.111
15	1.125	0.159	−0.826	0.117
16	1.139	0.163	−0.826	0.120
17	1.047	0.171	−0.718	0.121
18	1.003	0.178	−0.657	0.122
19	1.254	0.175	−0.893	0.131

5.5 $1s_5$ – $2p_9$ Transition (640.2 Nm)

At first glance, the $2p_9$ population can only radiatively relax back to the starting state $1s_5$, resulting in no changes in the population distribution among the $1s$ states, and thus no OG transitions should be observed. However, we did observe OG transitions following laser excitation. Collisions transfer population from $2p_9$ to other $2p$ state(s), which in turn relax down to $1s$ state(s), resulting in population distribution changes in the $1s$ states. The fitted parameters for the $1s_5$ – $2p_9$ waveform (shown in Fig. 4) are summarized in Table 6.

6 Results and Discussion

The stored data on the digital oscilloscope were fitted to the mathematical model and analyzed in this section of the work. Similar to previous experiments [5], Eq. (14) was used to fit the OG waveforms (index j replacing i in Eq. (13)):

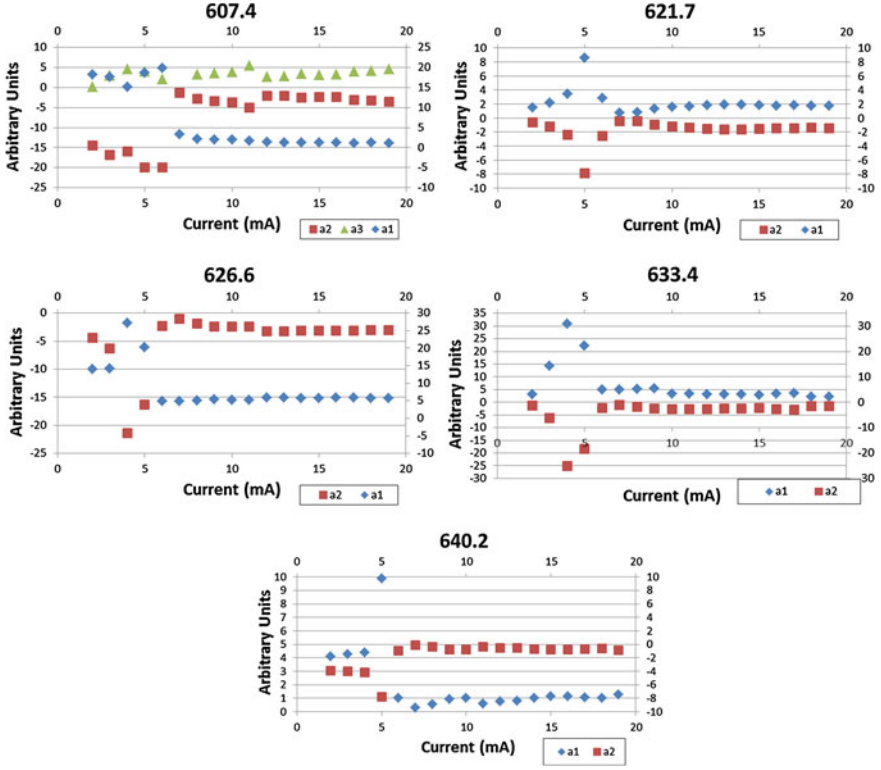


Fig. 5 Variation of the a-coefficients as a function of discharge current for the five OG transitions (607.4, 621.7, 626.6, 633.4, and 640.2 nm) studied for neon

$$S(t) = \sum_{j=1}^{j_{\max}} \frac{a_j}{1 - b_j} \left[e^{-b_j t} - e^{t/\tau} \right] \quad (14)$$

Furthermore, the parameters a_j , b_j and τ were obtained following least-squares fitting of each of the transitions $1s_i-2p_k$ using the above equation. The number of terms in the equation that were used to fit the waveform depended on the wavelength and the current. However, in most cases, not all of the four states were equally important and involved in a particular optogalvanic transition. As a result, we can fit the experimental signal using less than four terms in Eq. (14) for a particular optogalvanic signal, and the minimum case involved two states.

Of the several OG waveforms recorded in the present investigation: $1s_4-2p_3$ (607.4 nm), $1s_5-2p_7$ (621.7 nm), $1s_3-2p_5$ (626.6 nm), $1s_5-2p_8$ (633.4 nm) and $1s_5-2p_9$ (640.2 nm), two are shown for illustrative purposes in Fig. 4.

Figure 4 serves to illustrate the high quality of the Monte Carlo fits for the OG transitions studied for fixed circuit currents in the range 2.0–19 mA and also

demonstrates the variations in the amplitude and shape of the optogalvanic waveforms as a function of current and wavelength change. As a result of the interaction between the laser photons and the population in a specific $1s_i$ level, the neon atoms are excited to the $2p_k$ level, which in turn decays via spontaneous emission: $2p_k \rightarrow 1s_i$ ($i = 2, 3, 4, 5, \dots$), whereby the population of the initial $1s$ level decreases and one or more of different $1s$ levels increases. Depending on the ionization rates from these $1s$ levels, one observes an increase or decrease in ionization (with a corresponding increase or decrease in the OG signal) that lasts for varying lengths of time. As can be seen from Fig. 4, the values from the theoretical model are essentially identical to the experimental values. In Tables 2, 3, 4, 5 and 6, the fitted a-coefficients are in arbitrary units, while the b-coefficients are in units of $(\mu s)^{-1}$.

As seen from the above tables, the exponential rates, b_j , do not change significantly as the discharge current decreases from 19 to 8 mA. However, for 6 and 7 mA the exponential rates suddenly become very small. In addition, the tabulation shows a similar behavior for the a-coefficient as a function of the discharge current in the 19–8 mA range. Figures 5 and 6 help illustrate the rapid change in waveform behavior as the discharge current reaches 6 and 7 mA. It appears that there are

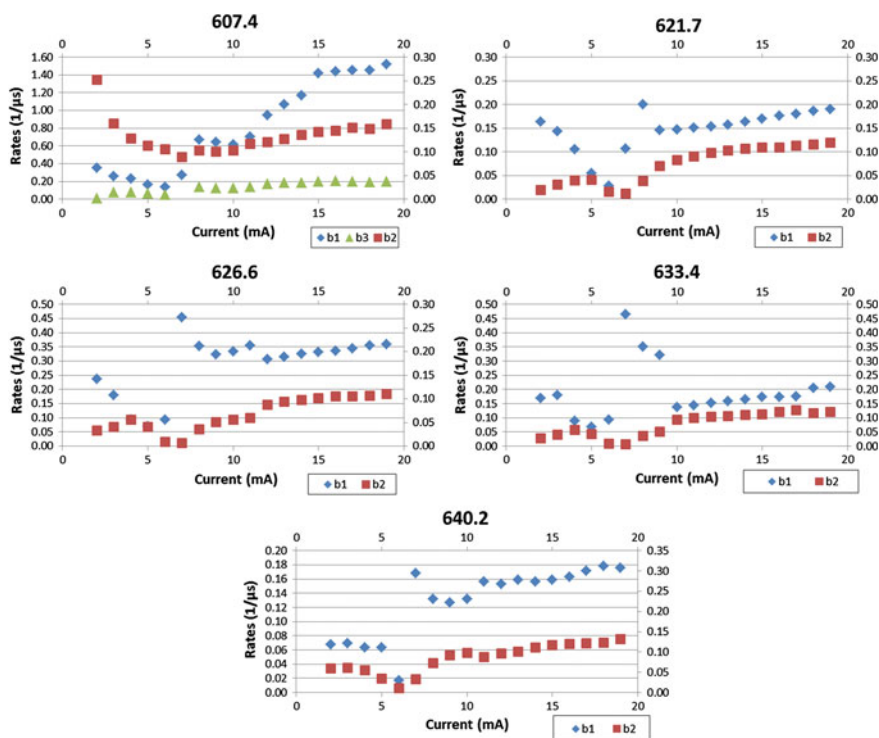


Fig. 6 Variation of the b-coefficients as a function of discharge current for the five OG transitions (607.4, 621.7, 626.6, 633.4, and 640.2 nm) studied for neon

noticeable plasma resonance effects around 7 mA, especially for the 607.4 nm transition, whereby our model is able to fit the experimental optogalvanic waveform with two terms only, as reflected in Table 2.

7 Concluding Remarks

In this chapter we have provided a historical perspective regarding the evolution of the optogalvanic effect and discussed both the experimental investigations and the mathematical formulation that helps explain the optogalvanic signal waveforms obtained by laser-exciting the discharge plasma in a hollow cathode lamp. In order to illustrate laser optogalvanic spectroscopy and collisional state dynamics associated with discharge plasmas, we have used a tunable laser to excite the plasma in an iron-neon (Fe–Ne) hollow cathode lamp and studied in great detail the neon transitions $1s_i-2p_k$ in the 590–670 nm region (for the current range 2–19 mA). Specifically, we focused on the following transitions: $1s_4-2p_3$ (607.4 nm), $1s_5-2p_7$ (621.7 nm), $1s_3-2p_5$ (626.6 nm), $1s_5-2p_8$ (633.4 nm) and $1s_5-2p_9$ (640.2 nm), to illustrate the applicability of the rate equation model developed and the excellent quality of the fit obtained employing the Monte Carlo fitting routine. The variations in the a- and b-coefficients as a function of current in the range 2–19 mA have also been determined and we noted a significant change in these parameters around 6–7 mA current values, while relatively small changes in the 8–19 mA range.

Current optogalvanic research continues to focus on the studies involving atomic states of various buffer gases, including metastable states, in a hollow cathode lamp employing a variety of electrode materials and gas combinations. Since the optogalvanic effect is driven by the change in conductivity of the plasma under the effects of a light source, studies such as the present one can provide insight into the use of laser optogalvanic spectroscopy in newly emerging fields, such as graphene-based nanoelectronics, nanoplasmonics and nanoplasma dynamics.

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