J. At. Mol. Sci.
doi: 10.4208/jams.051509.071209a

Vol. **1**, No. 2, pp. 118-125
May 2010

Collisional rate parameters for the $1s_4$ energy level of neon 638.3 nm and 650.7 nm transitions from the analyses of the time-dependent optogalvanic signals

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Received 15 May 2009; Accepted (in revised version) 12 July 2009;
Available online 19 April 2010

Abstract. A mathematical rate equation model using a Monte Carlo simulation has been used to analyze the laser optogalvanic signals of neon waveforms excited at 638.3 nm and 650.7 nm and arising from the $1s_4$ state transitioning to $2p_7$ and $2p_8$ states, respectively. The decay rates have been determined for the directly involved $1s_4$ state and also for the indirectly involved $1s_2$ and $1s_5$ states. There is good agreement among the decay rate constants found and they show a predominantly linear variation with increasing current.

PACS: 82.80.Kq, 87.10.Rt, 52.20.Hv

Key words: optogalvanic effect, Monte Carlo least-square fitting, collisional rates

1 Introduction

Laser optogalvanic spectroscopy has been established as an application tool for the measurements relating to ion mobility, atomic and molecular spectroscopy, ionization rates, and recombination rates, in the determination of velocity of particles and as a combustion probe for trace element detection. Optogalvanic (OG) effect is the change in the electrical impedance of plasma caused by resonant absorption of optical radiation by a plasma [1,2]. In the OG effect there is no problem of overlap from background emissions, and hence weak signals can be detected with a high signal to noise ratio, which makes this technique a very sensitive one to resolve vibrational changes in molecular bonds.

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Literature survey reveals that libraries of the OG transitions for neon are available in the visible region, and for argon in the UV region [3, 4]. There also exists a rate equation model [5–7] for the optogalvanic effect produced by tunable laser excitation of the neon 1s states in the positive column of a normal glow discharge. This model identifies quantitatively the dominant effects of electron collisional transfer and radiation wall losses and uses a non-linear least squares fitting procedure to obtain the relevant parameters. Recently we have utilized the Monte Carlo least-squares fitting method [8]to generate an accurate equation for modeling the OG waveforms. In the present study, a Monte Carlo fitting of the OG waveforms of neon associated with the $1s_4-2p_7$ transition at 638.3 nm and the $1s_4-2p_8$ transition at 650.7 nm for a variety of current values in the range 2-19 mA was utilized to understand the collisional processes and to estimate the parameters involved therein.

2 Experimental

The experimental set-up is shown schematically in Fig. 1.

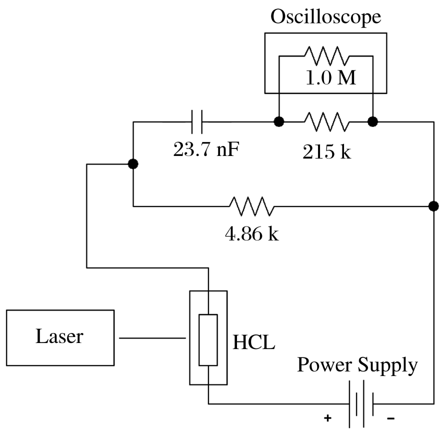

Figure 1: Schematic experimental arrangement for laser optogalvanic spectroscopy using a hollow cathode discharge lamp (HCL).

A pulsed laser (of typical pulse width 5 ns) is tuned to either the neon 638.3 nm or the 650.7nm transition and directed to enter a hollow cathode discharge lamp ("the galvatron" HCL) containing a mixture of Ne and CO gases. The galvatron is coupled in series with a current-limiting RC circuit, and the discharge current (2-19 mA) is controlled by adjusting the voltage on the power supply. The OG signal (deviation of the discharge current from its steady state DC value as a function of time) is displayed on a digital oscilloscope (Tektronix TDS 224; input impedance = 1.0 MΩ) and averaged over 256 pulses. The stored data is used for further analysis using a Monte Carlo fitting routine [7].

3 Results and discussion

In our laboratory we have carried out the spectral recording, and the subsequent analysis of the laser optogalvanic waveforms of neon and argon for different wavelength regions has been accomplished using the mathematical rate equation model that incorporates the various processes that contribute to the generation of the OG signals in the discharge plasma [9]. Recently, we have developed and used a robust and stable Monte Carlo least-squares fitting technique to simulate the optogalvanic waveforms optimally [8]. In the present work, we have chosen two neon transitions: 638.3 nm $(1s_4-2p_7)$ and 650.7 nm $(1s_4-2p_8)$ recorded at various discharge currents (2 - 19 mA) in order to validate the rate parameters of the initial states by our simplified rate equation and fitting technique.

The mechanism is displayed in Fig. 2 below. A laser excites molecules from level L_1 to L_2. Frequent collisions transfer molecules from L_2 to L_2'. Subsequently, molecules radiatively decay down to lower levels L_3, L_4 and L_5, achieving a different population distribution. The new population distribution will have a total ionization rate that produces a different discharge current.

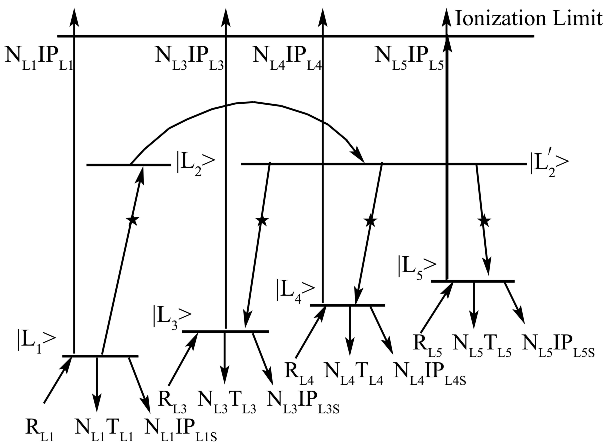

Figure 2: Energy-level diagram illustrating the optogalvanic effect.

The time-dependent optogalvanic signal is given by [4,8]

$$S(t)=\sum_{j=1}^{j_{max}} \frac{a_j}{1-b_j t}\left(\exp(-b_j\tau)-\exp(-t/\tau)\right), \tag{1}$$

where the amplitudes a_j and rates b_j are related to the various collision/radiation parameters associated with the plasma, and τ is a time constant. For the neon 1s-2p transition,employing the Paschen notation, there are four 1s states and ten 2p states, which yield a total of 30 allowed radiative transitions. A schematic representation of the 30 allowed transitions for the neon atoms between the s and p states, along with their corresponding wavelengths (Å) is displayed in Fig. 3.

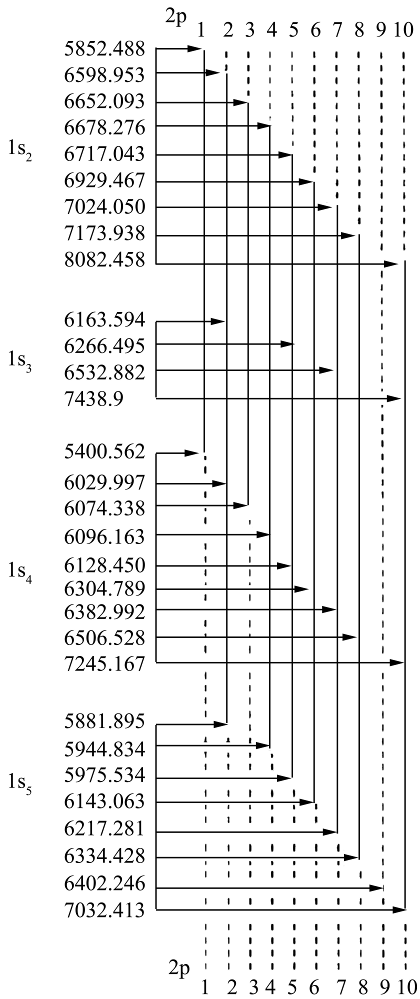

Figure 3: Schematic representation of the allowed transitions for the neon atom between 1s-2p (Paschen notation) states along with their corresponding wavelength (Å).

Of the four states involved, $1s_3$ and $1s_5$ are metastable with radiative lifetimes of the order of 1s, while the other two $1s_2$ and $1s_4$ decay to the ground state within $\sim$ 1ns.

In the present work, we have chosen 2 different transitions, namely $1s_4$ - $2p_7$: 638.3 nm and $1s_4$ - $2p_8$: 650.7 nm, in an effort to determine the rate constants of the initial state and the optically allowed decaying states. These transitions are recorded at various currents: 2-19 mA (forward) and 19-2 mA (backward) at 1 mA increments and a complete data set for each transition consist of 36 spectra. The waveforms were fitted to Eq.(2) by using a Monte Carlo least-squares fit

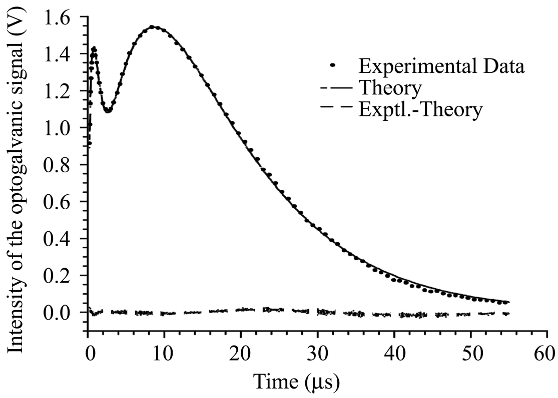

Figure 4: Observed and fitted optogalvanic waveforms of the neon transition at 638.3 nm for 10 mA current.

$$S(t)=\frac{a_1}{1-b_1\tau}\left(e^{-b_1t}-e^{-\left(\frac{t}{\tau}\right)}\right)-\frac{a_2}{1-b_2\tau}\left(e^{-b_2t}-e^{-\left(\frac{t}{\tau}\right)}\right)+\frac{a_3}{1-b_3\tau}\left(e^{-b_3t}-e^{-\left(\frac{t}{\tau}\right)}\right). \quad (2)$$

For each transition, the amplitude, rate constant and the time constant were determined. Let us consider each individual transition in turn and understand the process involved in obtaining the time-resolved OG waveforms.

3.1 $1s_4$ - $2p_7$ transition

Of the 30 allowed transitions shown in Fig. 3, we have chosen this transition at 638.3 nm because following laser excitation the excited neon atoms relax to optically allowed $1s_2$ and $1s_5$ states. Atoms in $2p_7$ can also relax to $1s_3$. Thus, in principle, we should see one more term for the optogalvanic transition. However, we do not see it because $1s_3$ is a metastable state, and the rate is small, whereby we do not fit in the long time region. By analyzing the waveforms, it is possible to obtain the decay rates for the $1s_4$, $1s_2$ and $1s_5$ states, as well as the positive and negative amplitudes and the time constant. The observed and the fitted time-resolved optogalvanic waveform for 10 mA current is shown in Fig. 4. According to the above mentioned scheme, the observed waveform can be fitted to the expression in Eq.(2). The values of the fitted constants are given in Table 1.

From Table 1 it is clear that the decay rate b_2 corresponds to the s_4 state, b_1 to the s_2 state and b_3 to s_5.

3.2 $1s_4$ - $2p_8$ transition

This particular transition exists around 650.7 nm, where the neon atoms after excitation can relax back to two states, namely $1s_2$ and $1s_5$, as seen in Fig 3. The observed and the fitted time-resolved OG waveform for 10 mA current is shown in Fig. 5.

Table 1: Fitted decay rates obtained from a non-linear least-squares fit of the observed OG waveforms for neon at 638.3 nm for 2-19 mA currents.

Current (mA)	$b_1(\mu s^{-1})$	$b_2(\mu s^{-1})$	$b_3(\mu s^{-1})$
2	0.689	0.137	0.033
3	1.056	0.159	0.050
4	1.498	0.111	0.072
5	3.845	0.071	0.054
7	2.348	0.177	0.051
7.5	2.216	0.155	0.066
8	1.067	0.122	0.086
9	1.165	0.131	0.094
10	1.238	0.170	0.087
11	1.880	0.165	0.099
12	1.815	0.165	0.107
13	1.908	0.183	0.108
14	2.205	0.185	0.116
15	2.010	0.190	0.120
16	2.369	0.203	0.132
17	2.525	0.217	0.136
18	2.657	0.258	0.135
19	2.838	0.334	0.133

Table 2: Fitted decay rates obtained from a non-linear least-squares fit of the observed OG waveforms for neon at 650.7 nm for 2-19 mA currents.

Current (mA)	$b_1(\mu s^{-1})$	$b_2(\mu s^{-1})$	$b_3(\mu s^{-1})$
2	1.071	0.138	0.031
3	1.404	0.166	0.045
4	2.191	0.121	0.071
5	3.556	0.089	0.068
7	1.219	0.097	0.057
8	1.111	0.128	0.078
9	1.484	0.136	0.088
10	0.868	0.168	0.084
11	0.952	0.162	0.094
12	1.122	0.154	0.107
13	1.229	0.161	0.113
14	1.442	0.162	0.121
15	1.721	0.166	0.128
16	2.094	0.175	0.133
17	2.235	0.180	0.140
18	2.210	0.186	0.149
19	2.481	0.192	0.153

The observed waveforms were fitted to the expression in Eq.(2) and the constants obtained are summarized in Table 2.

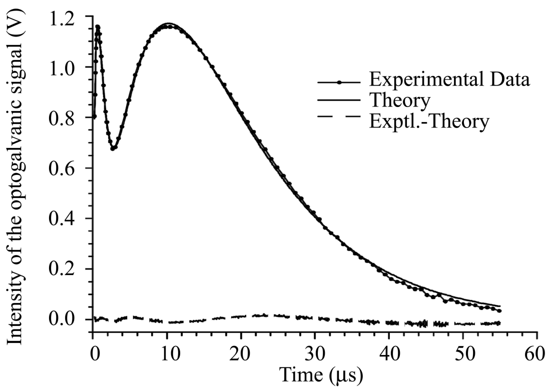

Figure 5: Observed and fitted optogalvanic waveforms of the neon transition at 650.7 nm for 10 mA current.

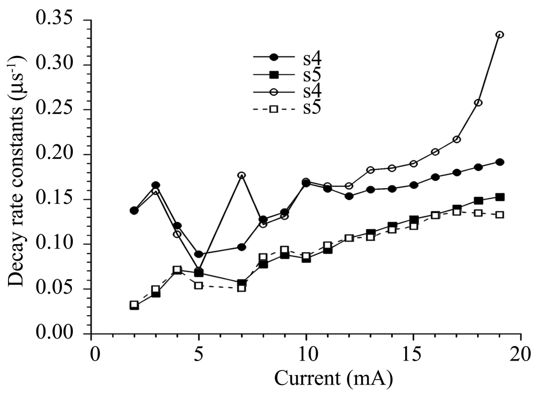

Figure 6: A plot of the rate constant versus current for the optogalvanic transitions associated with $1s_4$ and $1s_5$ states.

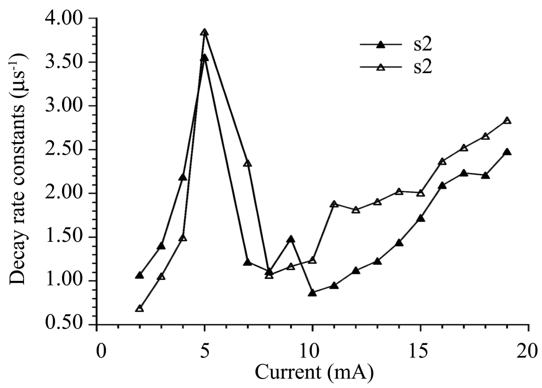

Figure 7: A plot of the rate constant versus current for the optogalvanic transitions associated with $1s_2$ states.

From Table 2 it is clear that the decay rate b_2 corresponds to the s_4 state, b_1 to the s_2 state and b_3 to s_5. In Figs. 6 and 7, the hollow symbols represent the 638.3 nm transition, while the solid symbols represent the 650.7 nm transition. A plot of the decay rate constants versus the current shown in Fig. 6 shows interesting characteristics pertaining to the $1s_4$ and $1s_5$ levels associated with the two neon transitions that have the same initial state $1s_4$. Similarly, a plot of the decay rate constants versus current for the $1s_2$ state is shown in Fig. 7. In this figure, the values of the rate constants for the $1s_2$ state shows similarity from the analyses of the neon transitions at 650.7 nm and 638.3 nm. Based on the present work, it is evident that one can estimate the rate constants accurately for the 1s levels involved either directly or indirectly. All of the rate constants show a predominantly linear variation with increasing current.

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