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Two-dimensional optogalvanic spectroscopy

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ABSTRACT

In this work, the time domain of optogalvanic signal is considered as an extra dimension for the analysis of the optogalvanic spectra. A time window was used to integrate over the different time regions of the temporal OG signals for each wavelength. The method enhanced the resolution of spectra considerably so that two closed transitions, which differ only by 4 pm, were precisely separated. In addition a new transition of Neon around 640 nm masked by a transition at 640.229 nm was observed and assigned using the new method.

1. Introduction

Optogalvanic (OG) effect is widely used as an effective and excellent spectroscopic method on species present in a discharge medium. This technique has a wide variety of uses such as wavelength calibration [1–3], atomic and molecular spectroscopy [4] and isotope enrichment [5]. It is relatively simple, and does not require complicated detectors, electronics and instrumentation. In fact, the impedance of the gas discharge itself is used as the detector. When a discharge is created in gas by an applied electric field, the excited electronic states of the atoms or molecules become populated to form a new steady state population distribution over all the states. When the discharge is illuminated by a laser beam with the wavelength in resonant with two excited states, the steady state distribution is changed. Consequently, the ionization rates and the impedance of the discharge are changed, which leads to a variation in the discharge current. In practice, a hollow-cathode lamp is used as the discharge source and the variation in the discharge current is measured while the laser wavelength is scanned. When the laser is pulsed, a sudden perturbation occurs in the discharge and results in a fluctuation in the current. If the laser pulse is shorter than the relaxation time of the discharge, the evolution of the perturbation can be followed. The time behavior of the fluctuation contains information about the states involved in the optogalvanic transition. A simplified theory of the OG signals in both cw and pulsed lasers was given by Erez et al. [6]. Several theoretical models have been developed and used for explaining the shape of the OG temporal signal [7–10]. Other researchers have proposed modified theoretical models to obtain quantitative information such as the collisional decay rate of the upper excited states, which has the main role in the shape of the OGs [11,12].

As the nature of the states involved in the transition forms the temporal shape of the optogalvanic signal, if two very close transitions overlap, the overall signal contains two sets of information corresponding to the two transitions. In fact, the signal is the sum of two separate signals with different time behaviors. The aim of this work is to discover this difference and refer that to different close transitions. In fact, the time evolution of

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the optogalvanic signals is used for further enhancement of the resolution of the OG signals without requiring additional experimental tools. It will be shown that two very close peaks, which are beyond the experimental resolution, could be well separated by putting a time window on a selected region of the temporal signal. By this technique we were able to separate two superimposed transitions at 667.828 and 667.832 nm, previously observed by Narayanan et al. using a different technique [13]. In addition a new one-photon transition of Neon around 640 nm, masked by a broadened transition at 640.229 nm, which has not been observed by previous researchers [13–15], will be reported.

2. The experimental setup

The experimental setup is displayed in Fig. 1. The photon source is a tunable dye laser (Quantel TDL-90, France) pumped by an Nd:YAG-laser (Quantel model YG-80, France) of 10 ns pulse width. The DCM dye was used to create a laser light in the range of 620 and 670 nm. The dye laser wavelength was scanned with a scan step of 0.002 nm using a commercial program provided by the manufacturer. The dye laser produced 100–200 μJ/pulse with the line width of 0.08 cm^{-1} corresponding to 3 pm at 600 nm. A wavelength meter (WS6-Highfinesse, Germany) was used to record the laser wavelength while recording optogalvanic signals. A commercial Ni–Ne hollow cathode lamp along with a home-made adjustable dc power supply (200–600 V) was used to create discharge in neon. The discharge current was controlled by a current limiting load resistor (100 kΩ). A ballast resistor (22 kΩ) was used to read the discharge current. The laser beam illuminates the plasma through the window on top of the lamp. The discharge current was adjusted between 1 and 10 mA. When the laser beam is resonantly absorbed by the plasma species, the voltage and current across the hollow cathode lamp will vary. The change in the current was coupled through a 0.01 μF capacitor and then fed to a digital oscilloscope (Picoscope ADC212, UK). The variation in voltage as a function of time was recorded for each laser shot. The voltage–time graphs were averaged over 30 shots for each wavelength. Then, the averaged voltage time graphs were integrated over a fixed time window for all wavelengths. The OG spectrum was finally obtained by plotting the integrations versus the wavelengths.

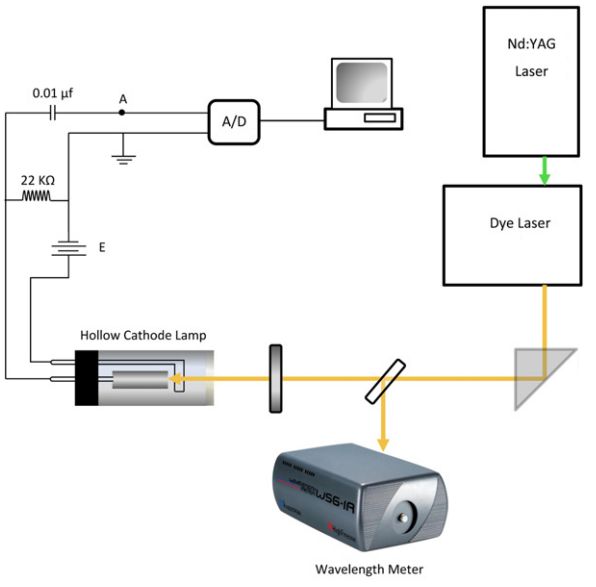

Fig. 1. Experimental setup for recording the OG signals. Voltage of the point A is read by the probe of an oscilloscope.

3. Results and discussions

3.1. The method

The typical OG signal at 630.480 nm is demonstrated in Fig. 2a. Following the laser shot, a sudden increase in the discharge current is observed, which is followed by a sharp exponential decay to negative part and a second increase; then, the current smoothly reaches its initial value. The wavelength was simply scanned in order to obtain a series of different OG signals at each wavelength, i.e. a three-dimensional plot, shown in Fig. 2b. The signal is integrated over certain time intervals (positive, negative or absolute overall) at each wavelength. This yields a peak, which corresponds to the transition between the two electronic states. The peak intensity and its sign depend on the time window for integration but its position is independent of the window width.

It will be demonstrated that there is additional information in the time domain that is lost if only the overall integral is considered. Here, a method is proposed for disclosing the details of the transition by a systematic partial integration of the time-resolved OG signals. For example, the signal presented in Fig. 2 was partially integrated over a time window of 5 μs at each wavelength. The window was moved over the whole range of the time and the integration was repeated. The partial integrations along with overall integral are shown in Fig. 3. The overall integration was obtained from the absolute values of the temporal signal. It is clear that the overall integral as well as other plots have similar Gaussian shape with the same peak position. However, a very narrower peak is observed among the plots, shown as inset in Fig. 3. The width of this peak is almost half of that for the overall integral; hence, an increase occurred in resolution.

Another type of time resolved optogalvanic signal at 614.308 nm is shown in Fig. 4a, where a change in the curvature of the negative part is observed around 50 μs. One may think of another transition close to the main transition. This can be examined by the step by step integration of this signal at each wavelength as shown in Fig. 4b. Here again, no difference is observed in the shape and position of the peak. In fact, the dependency of the additional structure on the wavelength is the same as that for other parts of the signal. This type of OG signals has been commonly observed and well described in literature [16,17] assuming several models. The additional feature is due to the involvement of other states in the relaxation process [17].