CHAPTER 3

EXPERIMENTAL DETAILS OF OPTOGALVANIC SPECTROSCOPY

3.1 INTRODUCTION

Optogalvanic spectroscopy (OGS) is one of the versatile techniques for elucidating the energy levels of atoms and molecules. Besides the experimental simplicity, the high signal to noise ratio has made it a very useful method for spectroscopic investigation\(^1\). As described in chapter 2, OG signal arises when impedance of a low pressure gas discharge changes in response to the absorption of radiation by atomic or molecular species present in the discharge. The resulting increase or decrease in ionization gives a measurable change in voltage across the discharge tube \(^2\). This voltage change is observed in all kind of discharges; like hollow cathodes, positive column, arc, microwave discharges, as well as in flames and plasmas. Generally, electrical impedance variation is controlled by collisional ionizations, involving optically modified states as well as the transport properties within the plasma. The plasma itself acts as a sensitive non-optical detector of the perturbation of states produced by the absorption of photons.

In general, the experimental aspects for observing OG effect consists of 1) highly stable electrical discharge medium with suitable electrodes, 2) optical excitation of various species in the discharge medium using tunable pulsed or cw laser and
3) detection of the resulting OG signal The interaction of radiation with the discharge will produce change in voltage which can be measured using appropriate detection systems. The experimental simplicity along with the remarkable sensitivity is the most important aspect of the OGS that makes it a versatile tool for many spectroscopic applications.

The choice of discharge cells for dc optogalvanic studies depend on the nature of experimental requirements and samples. In general, a discharge cell consists of two electrodes filled with gas at a few torrs of pressure. A stable dc voltage is applied to the electrodes in order to sustain the discharge. In principle, most of the metals in the periodic table can be used as the electrode material and any of the atomic or molecular gas can be used as the gaseous medium. Properties of both electrodes and gases have considerable influence in generating the OG effect. The discharge environment provides a relatively high effective electron temperature which is potentially important factor in generating the OG signal. The existence of the significant amount of excited state populations in the discharge enables one to observe transitions between excited states in this method.

Spatial and temporal measurements using both cw and pulsed lasers have played an important role in elucidating discharge mechanisms, energy storage and transfer pathways. The dynamical features of the OG effect can be studied using pulsed dye lasers.
Important features of the O6 effect is its positive or negative characteristics and the spatial dependence (i.e. the dependence of the O6 signal on the position where the laser beam interacts within the plasma) due to space wise distribution of the species in the discharge medium. Hence for most of the applications, the configuration of the cell must be such that the interaction of laser beam with the plasma should result in a maximum voltage change.

The cells commonly used for OGS are hollow cathodes, positive column and diode type glow discharges [5]. Both sealed types and continuous flow gas cells are employed. In general, most of the commercially available hollow cathodes are sealed type, provided with cylindrical hollow cathode and a ring anode filled with a rare gas at a suitable pressure. Even though, experiment is possible using this cells only for a fixed gas pressure at which the cell is sealed, the discharge noise due to pressure variations is negligible and are particularly useful for high resolution spectroscopic studies. Continuous-flow type cells are best suited for the study of gases and for the study of the dynamics of interaction of laser beam with the discharge. In this case, even though, there are some problems due to the presence of noise induced by random pressure fluctuations, a wide range of pressure can be employed. The cells with de-mountable electrodes are convenient to change or clean the electrodes, so that the problems associated with de-gasing effects on the
electrode surfaces can be minimized and hence even reactive gases can be investigated. The design criteria and performance of de-mountable hollow cathodes for high resolution spectroscopy of refractory elements [8,7], wavelength calibration [8,9] etc. have been reported by various workers. Discharge cell for laser induced OGS with a fully adjustable electrode position suitable for the study of molecular gases using both cw and pulsed laser excitation has been developed [10,11]. Discharges with plane electrodes and positive column or other types with suitable electrode configuration having minimum noise are also commonly utilized for various spectroscopic and analytic measurements [12-18]. The OGS effect has also been observed in commercially available indicator lamp [19], which is in general consist of two electrodes separated by a few mm of distance and filled with neon gas at a low pressure.

The commercial hollow cathode discharge (HCD) lamps are inexpensive and are readily available. However, their use is limited since the hollow cathode cup design is not appropriate and the buffer gas cannot be changed. See-through cylindrical hollow cathodes have to be used in order to get a well defined location of the probing laser beam. The design of a hollow cathode for high resolution spectroscopy must be optimized for a given element and transition.

Since the spectroscopic measurements are performed in a discharge environment, much care is necessary to reduce the
perturbations. The line broadening due to Doppler effects and collision between charged and neutral particles caused by the electric field are the causes of such perturbations. The major difficulties that arise during OG studies are due to the presence of random discharge noise as a result of fluctuations in current caused by the variations in gas pressure or applied voltage and the sputtering from the electrodes. The noise can be minimized by maintaining the gas pressure at a steady level and by using a highly regulated power supply. The noise due to sputtering from the cathode surface or arcing between the electrodes can be minimized by using clean and polished surfaces. Configuration of the discharge cell and the operating conditions will also considerably affect the discharge noise. The spatial dependence of the signal on discharge parameters can also lead to difficulties in signal detections. However, this is advantageous in certain plasma diagnostic studies.

3.2 DISCHARGE CELLS

3.2.1 Continuous gas flow positive column discharge cell

In certain cases, sealed cells are not suitable for prolonged use where de-gasing effects will upset the same experimental conditions. So it is better to use continuous gas flow de-mountable cells. This type of cells are best suited for molecular gases that react with electrode material in which case, the cell can be cleaned if necessary. A cell with adjustable
electrode position with respect to the probe laser beam would not only be advantageous in optimizing the generated signal, but would also allow the study of fundamental discharge mechanisms which produce signal of a particular polarity or its time evolution.

Fig 3.1 shows details of the de-mountable continuous gas flow discharge cell fabricated in our laboratory. It has been used for high resolution spectroscopic study of nitrogen gas. The electrodes, made up of stainless steel, are cylindrical in shape, placed at both ends of a Borosil glass tube having an inner diameter 6mm and length 5cm. Glass windows are provided at both ends on the other side of the cylindrical hollow electrodes. Nozzles made of stainless steel for gas inlet/outlet and for connecting pressure gauge are also provided. The couplings which are not in direct contact with the discharge are made with brass and all the joints are vacuum tightened by "O" rings. The inner surface of the electrodes are well polished and there is no sharp edges so that the arcing is eliminated. The separation between the electrodes is altered by choosing glass tube of appropriate length. A constant gas pressure is maintained by using needle and diaphragm valves which are provided at the inlet and the outlet sections of the cell.

The cleaned cell is first evacuated with a vacuum pump and then flushed by passing experimental gas. A digital pirani gauge is used for monitoring pressure (Vacuum Techniques Model VT
Fig 3.1 Continuous gas flow positive column discharge cell
1) stainless steel electrodes, 2) brass couplings, 3) gas inlet, 4) pressure gauge, 5) gas outlet to pump, 6) glass tube and 7) glass window

Fig 3.2 Continuous gas flow glow discharge cell with tungsten electrodes
The inlet and the outlet valves are adjusted to maintain a steady gas flow so that the gas pressure inside the cell remains constant. A well regulated dc high voltage is applied through a ballast resistance. The discharge is then run for a long time at a slightly higher current than the actual current at which the experiment is performed, so that the presence of impurities in the cell is minimized. The discharge noise is then monitored and the pressure of the gas is adjusted such that it is minimum. It is observed that for cell with electrode separation of 5 cm nitrogen gas at about 0.1 to 5 torr and the discharge current below 5mA, discharge noise is about 2mV.

3.2.2 Continuous gas flow discharge cell for photoemission study

For photoemission optogalvanic effect studies, we have used another continuous gas flow discharge cell with tungsten electrodes with an inter electrode separation of 1cm (fig 3.2). These electrodes are placed in a glass tube of inner diameter 1cm and length 15 cm with optical windows on both ends. Two side tubes of 0.6 cm inner diameter are also provided for the inlet of the experimental gas (N$_2$, NO$_2$ and Ar) and for outlet of the gas as shown in the fig 3.2.

3.2.3 Hollow cathode discharge lamp

Hollow cathode discharge (hcd) lamp consists of a ring shaped anode and a hollow cylindrical cathode filled with a buffer gas taken at about a few torrs [20]. Most of the
commercially available light sources are of this type and they serve as a convenient source of radiation with narrow spectral lines for most of the solid elements in the periodic table. The wide range of applicability of such a source lies in the fact that the emitting metal atoms are produced not by thermal evaporation as in most other sources but by the process of ion bombardment. When a discharge is struck in a hcd lamp, positive ions of the carrier gas are accelerated towards the hollow cathode and bombard the inner surface with sufficient energy to eject atoms of the cathode material. A certain number of metal atoms then diffuse away from the cathode surface into the central region of the bore where they may become excited by electron impact. The hcd is suitable not only as a source for emission lines of atoms but also as a reservoir of atoms for carrying out experiments on atomic resonance absorption and fluorescence.

In thermal methods, the temperature needed to produce plasma with a suitably high electron density varies greatly from element to element and in the case of refractory metals a temperature in the range of 2000K to 3000K are required. The absorption line, of any element in a vapor, produced by sputtering in a gas discharge are narrow and the broadening is predominantly by Doppler effect, with width closely corresponding to that at the ambient temperature of the gas (300K). Sputtering methods permit studies to be carried out in metastable atoms and ions, since they can be produced with sufficiently high density in the
discharge and the plasma sample to be investigated is more localized than that in other discharge configurations. The density remains very stable over a long period of time and can be adjusted in a well controlled manner by altering the discharge current.

In a low pressure gas discharge, the cathode is continuously bombarded by the energetic ions which have been accelerated in the high field of the cathode dark space and by fast neutral atoms produced by charge exchange. The bombarding ions and fast neutrals possess a wide range of kinetic energies. The species ejected during sputtering of a metastable target consists predominantly of ground state neutral atoms and a certain small fractions may also be in the form of excited atoms, ions and small clusters of atoms. The sputtered atoms rapidly lose their high kinetic energy of ejection by elastic collisions with rare gas atoms and become thermalized. Many of the atoms diffuse back to the cathode, while a small number of them escape towards the wall of the cells. As the sputtered atoms pass through the negative glow region some may get excited or ionized by electron impact or by collision with metastable atoms or ions present in the discharge. In this way, it is possible to accumulate neutral atoms, metastables and charged ions in a reasonably high density suitable for carrying out atomic absorption and fluorescence experiments.

Fig 3.3 shows the schematic diagram of the commercial hollow
cathode discharge lamp. The hcd we used are commercially available Ne/Nd and Ne/Mo lamps (Cathodean UK) which consist of a bulb having a glass window into which a hollow cylindrical cathode and a ring shaped anode have been inserted. The atmosphere within the bulb consists of neon gas at a pressure of 10 Torr. The construction has been designed to increase the negative glow there by achieving a high spectral intensity. With a suitable voltage applied between the electrodes of the hcd lamp, a glow discharge occurs. Electrons pass from the interior of the cathode to the surface of the hollow cathode region towards the anode. This causes ionization of the gas within the lamp through non-elastic collision with the gas atoms. Positive gas ions are accelerated by the electric field and collide with the cathode surface. The kinetic energy of the ion causes material to be sputtered from the cathode surface in the form of single atoms which are at the lowest energy or ground state. Simultaneously, electrons accelerated by the electric field towards the anode collide with ground state metallic atoms so that they are excited to higher energy states. The excited atoms de-excite to the lower state emitting spectral line characteristic to the element. In addition to this, radiation due to the transitions corresponding to the buffer gas atoms in the lamp are also obtained. Intensity, stability, noise and spectral profile etc. are strongly influenced by the nature of the gas, pressure, the element used for the cathode and its
Fig 3.3
Hollow cathode discharge lamp
A-ring anode,
C-hollow cathode

Fig 3.4
Neon glow discharge indicator lamp
A-ring anode,
C-disk cathode
surface state, the electrode construction, discharge current and the applied voltage.

3.2.4 Glow discharge indicator lamp

OG effect in commercially available indicator glow discharge lamp filled with neon and argon gases has been reported [19,21]. While the OG resonances of these discharges are of some spectroscopic interest, the primary motivation for the investigation lies in the use of these lamps as calibration devices for tunable dye lasers. These lamps, in general, consist of two electrodes very close to each other, filled with rare gases at a reduced pressure and usually operated at very low voltages showing the characteristic glow of the fill gas. We have used an indicator lamp having ring shaped anode and a disk cathode (of diameter 1cm) with an inter electrode separation of about 2.5 mm in which neon gas is filled as the discharge medium (fig 3.4).

3.2.5 High voltage power supply

One of the serious problem that limit the sensitivity in OG experiment is the presence of large discharge noise due to random fluctuations in the pressure or current. This can arise as a result of variations in gas pressure or the applied voltage, presence of impurities, sputtering from the cathode etc. Hence it is essential to maintain the discharge with a minimum noise using an extremely stable and ripple free voltage source. The voltage source used is a stable well regulated high voltage power
supply having very low ripple factor (2mV peak to peak), and the output controllable from 100V to 2800V up to a maximum current of 5mA (Thorn EMI PM288) [22]. The unit is provided with a switch controlling the output in 200 V steps from 100 - 2300 V and a five turn potentiometer for fine voltage control giving range of 0 - 500V.

3.3 OPTICAL EXCITATION SYSTEMS

3.3.1 The cw laser source

I) Argon ion laser

The cw laser used is a 12 Watt argon ion laser (Spectra Physics 171) capable of providing discrete lines of wavelength 514.5, 496.5, 488, 476.5 nm etc or a multiline output containing all the lasing wavelengths [23]. The discrete lines can be obtained by tuning the prism which is placed in the cavity. The output has a gaussian profile and has a frequency stability 60 MHz/°C and a stability of ± 0.5% when used in the light control mode. The laser is also provided with power meter to continuously monitor the output power.

II) Single mode ring dye laser

For tunable laser output, which is very important for OGS, radiation from Spectra Physics 380D ring dye laser [24] pumped by above argon ion laser is used (fig 3.5). The ring dye laser has a travelling wave, ring resonator with tunable high power, single frequency radiation. The ring resonator consists of a pump
mirror, which focuses the pump laser beam into the dye jet and has four additional mirrors which constitute the cavity. In the cavity, the beam travels in a pattern of figure eight. A unidirectional device which introduces a directional anisotropy into cavity is used to select a particular propagation direction. The output power is concentrated in a nearly single frequency beam with a narrow line width. Because the emission gain curve of the lasing dye extends over several nanometers, simultaneous lasing can occur at a large number of cavity mode frequencies. Single frequency selection is achieved by using a birefringent filter with a fine etalon (FSR = 900 GHz) and an electrically tunable single frequency etalon (FSR = 75 GHz). The spectral range of these three selection elements are such that loss is introduced for all other cavity modes except the particular one where lasing is desired.

To scan the output frequency, the cavity modes with a spacing of about 200 MHz are tuned by changing the length of the laser resonator using two galvoplates. The index of refraction of the plate is higher than that of air, there by changing the effective cavity length. By scanning the inter etalon separation at the same rate as the dual galvoplates scan the cavity mode frequency, the output frequency of the single frequency dye laser can be scanned.

Stabilock system is used to achieve narrow line width and to avoid mode hops during scanning. The dye laser frequency is
stabilized by locking it to a fringe of an external reference interferometer (FSR = 0.5 GHz). Frequency deviations are detected by an error signal fed back to the PZT maintained mirror M2 and the galvoplates. When the laser try to hop the mode, another 10 GHz interferometer circuitry takes up and returns the laser frequency to the correct fringe and then the frequency control hands over to the 0.5GHz interferometer.

The tunable range of this laser with Rh6G dye is from ~570-600 nm having line width of a few MHz and the output
power/wavelength are extremely stable. The continuous tunability over a wide spectral region, narrow line width and the stability of this laser system has made it very suitable for high resolution spectroscopy.

3.3.2. The pulsed dye laser

Pulsed dye laser source used in the present studies is Quanta Ray PDL 2 dye laser system in which Rh 6G is taken as the lasing medium. It is pumped by the second harmonic output at 532nm of a Q-switched Nd:YAG laser (Quanta Ray DCR 11) \[25,26\]. This dye laser provide a continuous wavelength output from 540-580 nm peaking at ~564nm. Wavelength tuning is performed by a stepper motor attached to the grating element with a minimum speed of 0.04nm/step. The wavelength reading is obtained from the factory calibrated readout provided on the dye laser assembly.

3.4 DETECTION SYSTEMS

I) Wave-meter

The Burleigh WA-20 VI wave meter is used for the measurement of the wavelength or frequency of the cw laser. Using this instrument measurement with an accuracy of 0.01 cm\(^{-1}\) can be made. It consists of a scanning Michelson interferometer coupled to a fringe counting system. The wavelength or the frequency determination is made by counting number of fringes of the input laser beam simultaneously that of the reference He-Ne laser for
which the wavelength is accurately known [27].

In a typical experimental setup, a small portion of the laser to be measured is coupled into the wavemeter by a beam splitter. The alignment of the laser to the wavemeter is facilitated by the tracer He-Ne laser beam from inside of the wavemeter. Continuous automatic monitoring of the laser wavelength can be performed while the laser is tuned. If the indicating wavelength is incorrect, the display will not update and will show some error message on the wavemeter. Only a very low power (0.1mW) of the sample laser beam through the 2mm input aperture is required for accurate wavelength measurements and this can be tapped from the main beam with only negligible loss.

II) Spectrum analyzer

Spectrum analyzer (Spectra Physics 470) [28] is a mode degenerate spherical mirror Fabry-Perot interferometer used as a scanning spectrum analyzer for high resolution optical spectroscopy. Its operating range is 550-650nm and the separation between the adjacent transmission maxima (free spectral range) is 2 GHz. A free spectral range will be scanned in the time required to change the mirror separation by 1/4 wavelength. Using Spectra Physics 476 scanning interferometer drive [29], the spectral dispersion, position of the displayed spectra, repetition rate and amplitude can be varied over a continuous range. Since the free spectral range of the spectrum analyzer is known to be 2 GHz, the repetitive feature of the
display can be used to calibrate the observed spectrum which is very important in high resolution spectroscopy.

III) Laser energy meters

The laser energy/power that is used in the experiments is measured by using laser power meters (Scientech model 382 and EG&G model 480-1A) [30,31]. Usually the measurements are taken in the main beam path before or after the experimental data has been recorded.

IV) Monochromator

A monochromator system essentially contains an entrance slit, a collimator, a dispersive element (in the present case a grating), a second mirror or lens to focus the dispersed light and an exit slit. The height and width of the slits are generally variable. Jarrell-Ash (Model No. 5) is a 0.5m grating monochromator having a maximum resolution of 0.02nm. This instrument provides smooth scanning motion in eight speeds ranging from 0.2nm/min to 50nm/min. The output from the Jarrell-Ash monochromator is detected by an EMI model 9683 KQB photo multiplier tube that can directly mounted at the exit face of the monochromator. Model 9683 is a head on type PMT having S-20 cathode and performs well in the 300-800nm region.

V) Modulation

Modulation of the incident laser beam is essential for the detection of the OG signal. For cw source, mechanical choppers EG&G 192 and Stanford SR 540 [32,33] are used to square wave
modulate the intensity of optical signals. The modulation frequency output is provided as reference to lock-in amplifier.

VI) Oscilloscope

To monitor the signal 20 MHz analog oscilloscopes (L&T, Aplab) and 200 MHz digital storage oscilloscope (Iwatsu DS-8621) are used. The digital storage oscilloscope has signal averaging and data storing facilities which can also be used to obtain hardcopy of signal shapes using plotter/printer [34].

VII) Lock-in amplifier

Lock-in amplifiers are used to detect and measure very small AC signals accurately. It uses a technique known as phase sensitive detection in which signal at frequencies other than the reference frequency are rejected and do not affect the measurement. Typically in an experiment, the sample is excited at a fixed frequency (this reference signal is a square wave from the mechanical chopper) and the lock-in detects the response from the experiment at the reference frequency. Only the signal at the reference frequency will be processed and a voltage proportional to the rms signal amplitude is obtained as the output. For the present measurements we have used two lock-in amplifiers, EG&G 5208 [35] which is computer interfaced with RS 232 and SR 850 [36] which has disk drive facility for data storage.

3.5 GENERAL EXPERIMENTAL SET UP

General scheme of experimental setup (fig 3.6) consists of
the measurement of galvanic effect produced in the electrical discharge by the absorption of laser. Commercial hollow cathodes, neon indicator lamp and home made continuous gas flow cells with N₂ gas or tungsten electrodes/N₂, NO₂ and Ar gas discharges are used as the discharge medium. A current limiting resistance and a milliammeter are connected in series with the cell and the discharge is maintained by applying a stable dc voltage. The discharge condition is adjusted by varying gas pressure, applied voltage etc. so as to get a minimum electrical discharge noise. Radiation from the pulsed dye laser or intensity modulated cw laser is passed into the cell. For OG studies laser beam is passed without falling on the electrodes so
that the photoelectric emission is completely eliminated while for photoemission optogalvanic measurements the beam is allowed to fall on the cathode surface. The AC signal is measured with CRO, lock-in etc. by blocking the dc voltage with a capacitor. Measurement were carried out by monitoring laser wavelength, laser power, gas pressure, discharge current, spatial position where the laser beam is interacted within the discharge etc. Specific details about the experimental aspects are discussed in the subsequent chapters.

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