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REVIEW PAPER

Laser Optogalvanic Spectroscopy : Experimental Details and Potential Applications in R&D

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ABSTRACT

Laser Optogalvanic Spectroscopy (LOGS) is an extremely sensitive detection technique based on the 'Optogalvanic Effect'. The impedance change of gaseous discharge following the absorption of resonant laser light by the discharge species has proved to be a powerful spectroscopic tool to investigate all kinds of matter in vapour phase in discharge plasmas and flames. LOGS does not require any optical detector and the signal-to-noise ratios are often greater than 10^3. The advent of tunable lasers has pushed LOGS as a unique detection technique, efficient over a wide frequency spectrum from UV through visible to IR. As a simple and most sensitive detection technique, LOGS can have diverse practical applications in science and technology. The experimental details with different discharge excitations and the potential applications of LOGS are briefly described. Some prominent practical applications like wavelength calibration, laser linewidth determination, trace element detection, isotope analysis, material characterisation, laser frequency and power stabilisation, Rydberg atom spectroscopy and combustion and plasma diagnostics are briefly discussed.

1. INTRODUCTION

All the applications of optical spectroscopy to R&D problems in science and technology, in general, require either spectral intensities of absorbed or emitted radiation or measurement of radiation-induced effects. In practical applications, a major limitation is commonly imposed by the attainable detection sensitivity. The question of how few atoms, ions, molecules or photons can still be detected at reasonable signal-to-noise ratio is of crucial importance for the successful solution of a given problem.

The introduction of laser as a spectroscopic tool has dramatically altered the field of optical spectroscopy. It has not only renewed the conventional optical spectroscopic techniques but has also led to the development of many powerful new spectroscopic techniques, both linear and nonlinear in nature. Several interesting properties of lasers, such as intensity, monochromaticity, coherence, polarization, short pulse widths, and tunability, make it possible to investigate the spectroscopy of even the transient species with many orders of magnitude more sensitivity and selectivity than was possible previously. High spectral density and purity of lasers have enabled the development of important nonlinear and sub-Doppler spectroscopic techniques which have achieved unprecedented precision measurements. But, the advent of dye-lasers has given a new impetus to almost all the spectroscopic techniques, particulary laser-induced fluorescence (LIF), laser optoacoustic detection (LOAD) and laser optogalvanic spectroscopy (LOGS) techniques. With all the above-mentioned qualities, the laser spectroscopic techniques provide us with a unique opportunity for accurate non-intrusive measurements with high spatial and temporal resolution even on extremely hostile media constituted by burning or exploding gases.

2. OPTOGALVANIC EFFECT AND ADVANTAGES OF LOGS

Optogalvanic spectroscopy (OGS) works on the basis of the 'Optogalvanic Effect' which is the change

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in the impedance of a gaseous discharge due to the resonant light absorption by the discharge species. It is simple and inexpensive but a powerful and very convenient detection technique for spectroscopic investigation of atoms, ions, molecules and radicals in all kinds of electrical, and high frequency (RF & microwave) discharge plasmas as well as flames over a wide spectral range[1-3] from UV through visible to IR.

LOGS is a very sensitive spectroscopic technique that enables the detection of the weakly absorbing transitions which are generally eluded in absorption and fluorescence. Unlike emission and absorption spectroscopy which require the use of optical detectors, OGS does not require any additional detector. The discharge plasma itself acts as a sensitive non-optical detector of the optical phenomena. No monochromator and no background filtering is needed in LOGS and the signal-to-noise ratios vary from 10^3 -10^5 depending on the type of discharge excitation.

The detailed quantitative description of the optogalvanic effect is perhaps difficult mainly because it is impossible to give a complete set of rate equations for all the levels and processes involved in the discharge. However, a qualitative explanation of the optogalvanic effect is fairly straightforward. In fact, the quantitative explanations are also possible for specific transitions by considering only the prominent levels whose population are greatly perturbed by the resonant light absorption[4,5]. There are two significant different mechanisms for the origin of optogalvanic effect in hollow cathode discharges[6]. In the first mechanism, the absorption of laser radiation in the discharge results in a change in the steady-state population of bound atomic or molecular levels. Since different levels will have different ionization cross-sections or ionization probabilities, a perturbation to the steady-state situation results in a net change in the discharge current or equivalently a change in the discharge impedance. In the second mechanism, the excitation of atoms or molecules by the laser to higher electronic states perturbs the equilibrium established between the electronic temperature and the atomic excitation temperature. But the superelastic collisions between electrons and the laser-excited atoms in the discharge immediately tend to restore the equilibrium. In this process, an excess amount of energy is released which often ends up in an increased electron temperature of the discharge. Therefore, the laser excitation of atoms leads to increase in the conductivity or decrease in the impedance of the discharge. In fact, both the mechanisms are expected to be present simultaneously in OGS. The relative importance of these two mechanisms depends on different discharge and excitation conditions.

The relative magnitudes, signs, and time evolution of the optogalvanic signals can be explained[7] qualitatively without any problems. The optogalvanic signals are usually negative. The absorption of radiation in the discharge produces a transition to a higher state, from which collisional ionization proceeds more easily and hence the discharge impedance and voltage across the discharge tube decrease. This represents a negative optogalvanic signal. Conversely, excitation from metastable states produces positive optogalvanic signals. Depletion of long-lived states from which the atoms can be ionized more easily by collisions leads to an increase in the discharge impedance and voltage across the discharge tube Actually the relaxation times are very sensitive to the plasma conditions. Increasing current or pressure can change the sign of a signal from positive to negative due to a decrease in T_1 (lifetime in lower state) caused by enhanced electron collisions. The time profile of an optogalvanic signal generally looks the same as that of I_{12} (intensity profile). In the small signal limit, the magnitude of the optogalvanic signal will be proportional to $(N_1\text{-}N_2)$ and $\sigma_{12}\, I_{12}$.

3. EXPERIMENTAL DETAILS WITH DIFFERENT DISCHARGE PLASMAS

Optogalvanic spectroscopy can be performed on all kinds of DC and pulsed discharges using either CW or pulsed lasers.

3.1 Hollow Cathode Discharge

The hollow cathode discharge serves as a rich reservoir of sputtered atoms. Under the right conditions of gas pressure and bore diameter of the cathode, the negative glows from opposite walls of the inner surface of the hollow cathode coalesce to produce neutral and excited atoms and ions in high densities at the centre of the hollow cathode[8-10]. The hollow cathode discharge is highly self-sustaining as it sustains large currents at the cathode-fall potential of only a small voltage.

Applying a potential difference of a few hundred volts between the two electrodes leads to breakdown

of the rare gas at low pressure and creation of a number of electron-ion pairs. The ions, accelerated in the high field of the cathode dark space, bombard the cathode material together with fast neutral atoms produced by resonant charge exchange. The high energetic ions and fast neutral atoms impart sufficient energy to the crystal lattice of the cathode material to dislodge and eject the atoms from the lattice sites. The sputtered species, predominantly single, ground-state neutral atoms, which initially possess high kinetic energies, rapidly lose their kinetic energy by elastic collisions with rare gas atoms and come into thermal equilibrium. As the sputtered atoms diffuse from the cathode surface into the negative glow, some of them are excited or ionized by electron impact or by collisions with metastable atoms or ions present in the discharge. In this way, reasonably high steady-state densities of ground-state atoms, metastable atoms and singly-ionized ions can be accumulated in the nagative-glow region of the discharge suitable for carrying out optogalvanic spectroscopy[11].

The experimental arrangement used for LOGS in a hollow cathode discharge is shown in Fig. 1. An all-line 5 W argon ion laser pumps a standing-wave cavity dye laser with flowing Rhodamine-6G dye solution. It produces a typical dye laser output power of 600 mW in the wavelength range 565-640 nm. The chopped dye laser output is focussed into the hollow cathode of a *U/Ne* discharge lamp by a condensing lens. The chopping frequency is chosen such that the noise is minimised in phase sensitive detection. Smooth scanning of the laser wavelength was accomplished by rotating the micrometer of the birefringent filter in the dye laser cavity by an 1/2 rpm synchronous motor. The optogalvanic signals which result as the voltage changes across the 10 kΩ ballast resistor were picked up through a DC-blocking capacitor of 0.1 μF and a fast over voltage protection (FOP) circuit and were fed to the voltage input terminal of a lock-in amplifier. The lock-in amplifier amplifies the signals which appear at reference frequency and are in-phase with reference signals and averages out all the asynchronous signals which mostly constitute the noise. In this way, a significant increase in the signal-to-noise ratio is obtained. The analog output of the lock-in amplifier is fed to a strip chart recorder. Fig. 2 shows a part of the recorded optogalvanic spectrum of uranium and neon. The saturation effects of uranium optogalvanic signals are shown in Fig. 3.

3.2 Positive Column Discharge

Positive column is the region of glow discharge characterised by spatial uniform brightness. Optogalvanic effect in the positive column of a rubidium

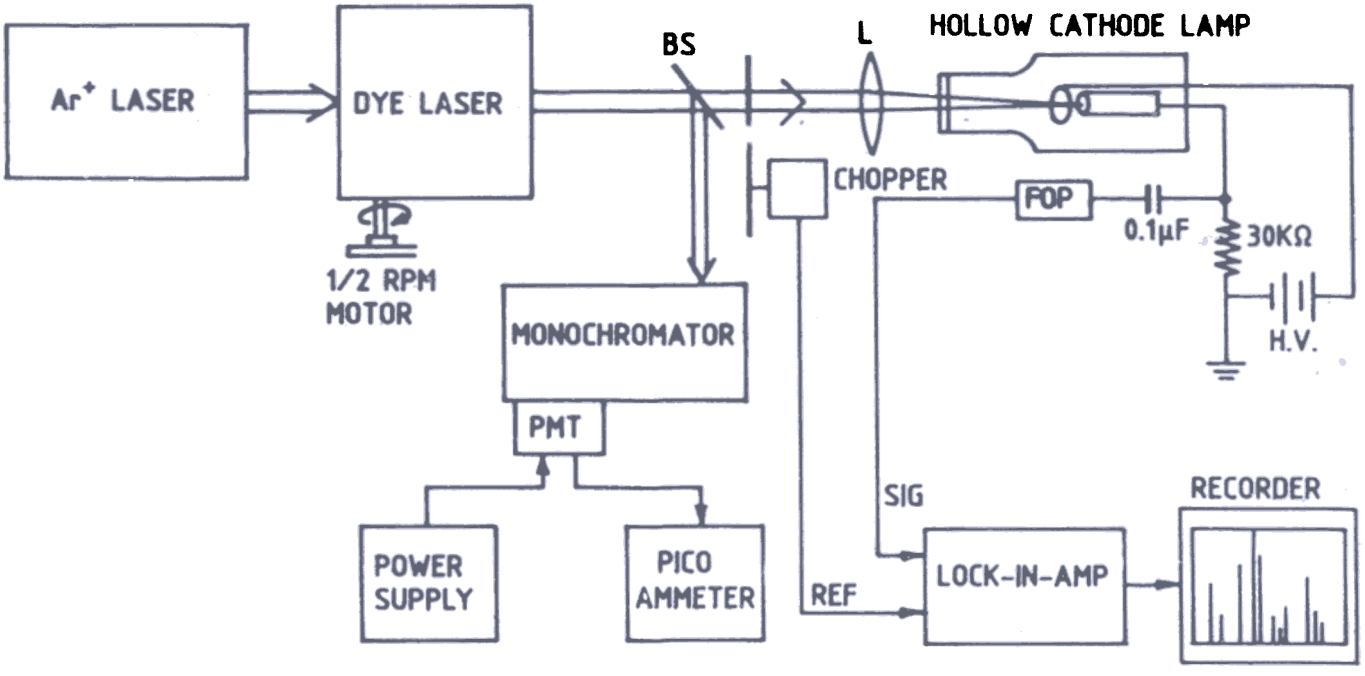

Figure 1 Experimental set-up of LOGS of uranium hollow cathode discharge. FOP-fast overvoltage protection; PMT-photo- multiplier tube

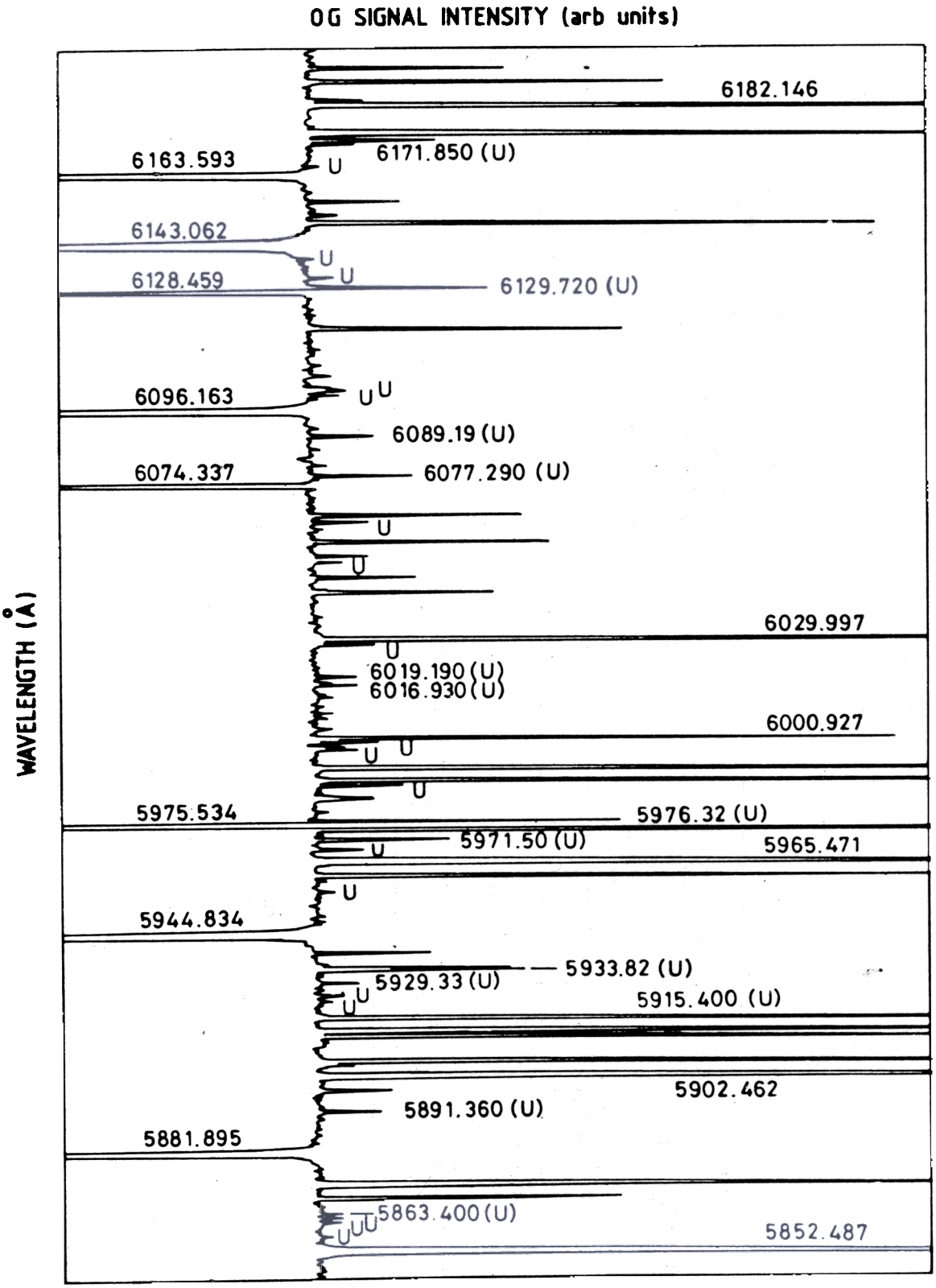

Figure 2. A portion of the recorded optogalvanic spectrum of uranium. Only the strong neon spectral lines used for wavelength calibration are identified.

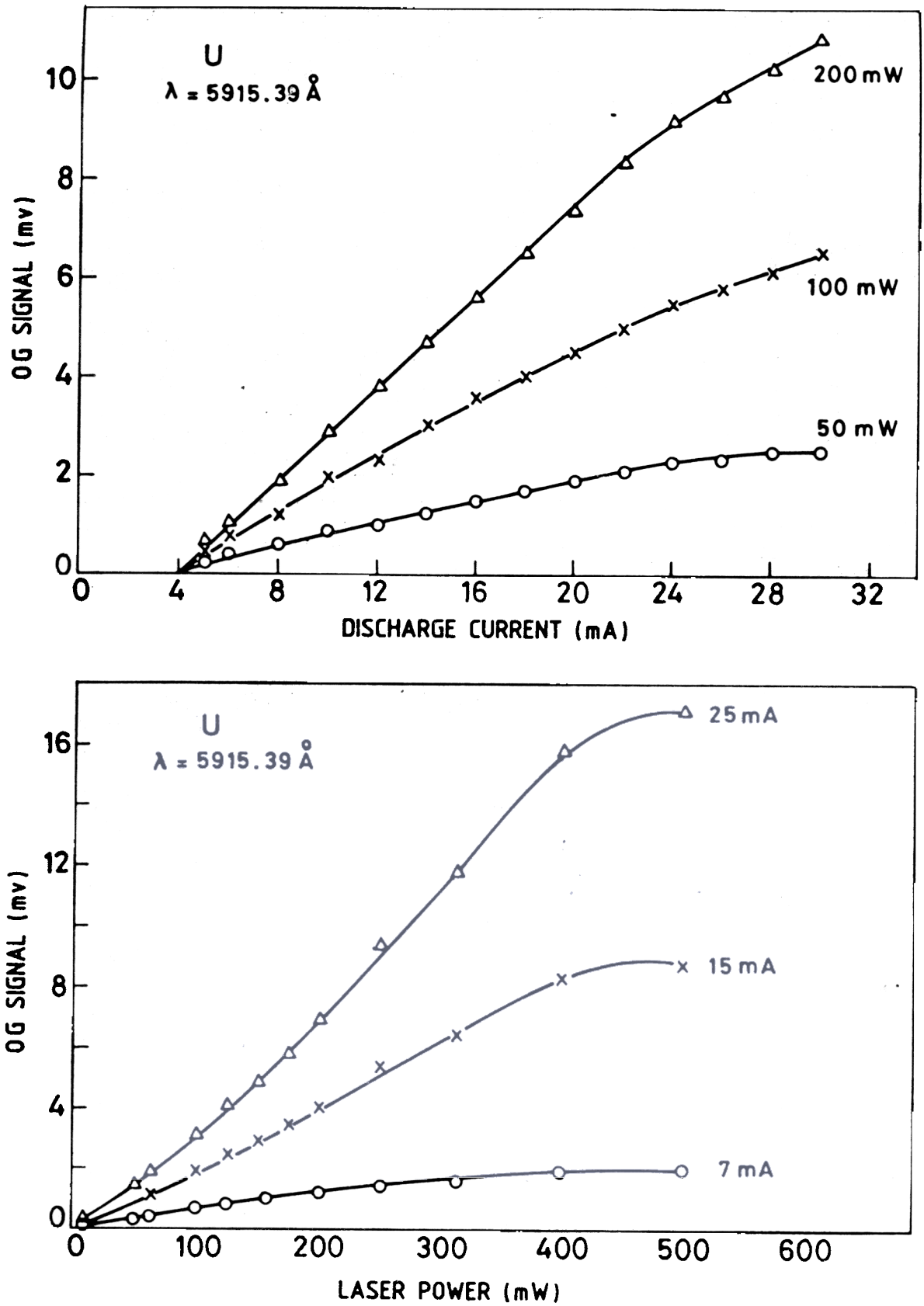

Figure 3. The typical saturation effects of uranium optogalvanic signals in a hollow cathode glow discharge on discharge current and laser power.

DC glow discharge was studied[12] using LOGS. A discharge tube with 4 mm internal diameter and a 10 cm active length between two stainless steel electrodes was constructed with pyrex glass. It was evacuated to 10^{-6} Torr and then filled with liquid rubidium and neon at 1.4 torr. A stable *Rb* gas discharge consisting of mainly a positive column was obtained over a current range of 6–9 mA at a cell temperature 200 °C. The experimental arrangement is shown in Fig. 4. The dye laser beam was chopped at 320 Hz to get good signal-to-noise ratio. Cesium present in the *Rb* impurity trace gives rise to *Cs* spectra in the Rydberg series $5d^2D_{3/2,5/2}\ nf^2F_{5/2,7/2}$ ($11 \leq n \leq 23$). All the seven single-photon transitions of *Rb* expected in the range were studied and a few two-photon transitions are observed.

evacuated and filled with *Rb* (about 2 ml) and *Ne* at a pressure about 0.4 torr. At the resonant frequency of 33 MHz, a pink uniform discharge of *Rb* was struck. The optogalvanic signals of both *Rb* and *Ne* were obtained as a change in the voltage across load resistor R_1 of the oscillator.

3.4 Flame and Flame-like Discharges

Since the flame is a chemically sustained mild plasma, LOGS can be conveniently employed on any analytical flame to investigate atoms, molecules and free radicals. The typical experimental set-up using a pulsed dye laser is shown in Fig. 6. An analytical flame is produced for the experiment by a slot burner. A pair of tungsten rods which are placed symmetrically around the flame act as the cathode while the grounded slot burner head acts as the anode. The cathode is held at

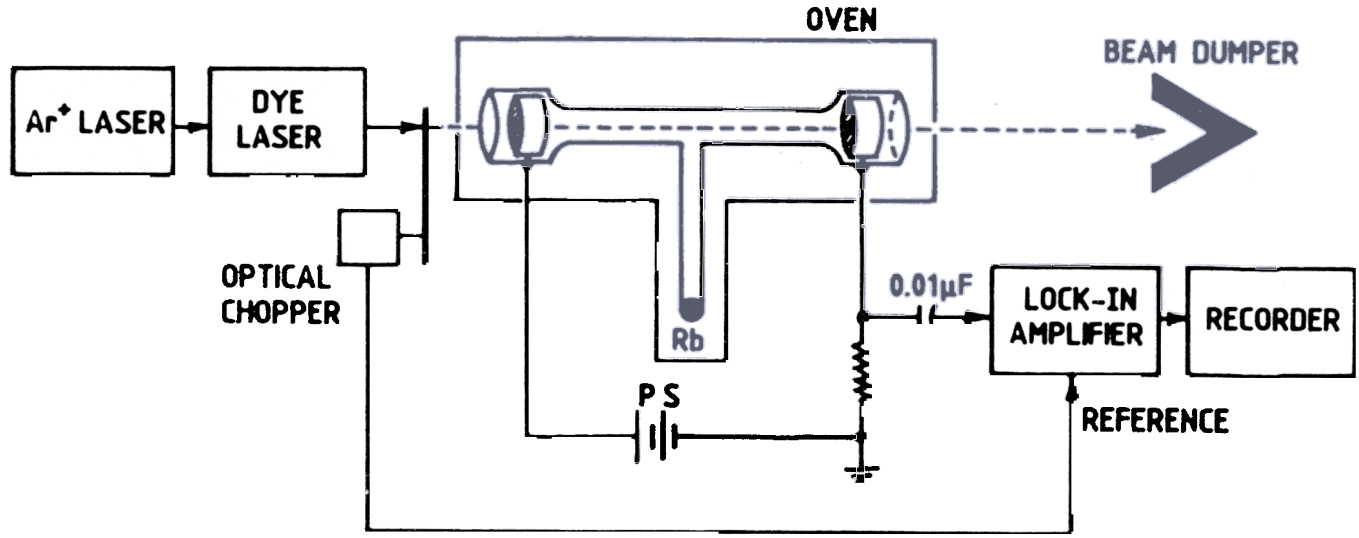

Figure 4. Experimental set-up of LOGS on rubidium positive column discharge.

3.3 Radio-frequency and Microwave Discharges

If a low-pressure gas or vapour cell is placed in a coil or capacitor comprising a part of resonant circuit coupled to a RF oscillator, a very uniform and noiseless discharge plasma is produced by driving the oscillation amplitude to the point of electrical breakdown. The high frequency discharge plasmas usually sustain the higher electron temperatures compared to DC discharges and thus a significant population of the excited states. Electrodeless discharges are particularly suitable for spectroscopic studies of scarce or corrosive gases.

The LOGS set-up using a Colpitts regenerative oscillator[13] with a triode 6AF4 is shown in Fig. 5. A pyrex glass tube 6 cm long and 1 cm in diameter was

a typical negative potential of 1 kV relative to the anode. The nitrogen pumped dye-laser beam is focussed on the flame between the electrodes and is tuned to the resonance of various transitions of the discharge species. The induced perturbation of the thermal population of energy levels results in the enhanced rate of collisional ionization and thus leads to the optogalvanic effect. This is the precise reason for which the LOGS in the flames is popularly called as Laser Enhanced Ionization (LEI)[14]. Double resonance step-wise excitation schemes can considerably increase the sensitivity of the technique. The pulsed optogalvanic signals are amplified and filtered before they are fed to Boxcar averager which averages the signal over 50 laser pulses to enhance the signal-to-noise ratio.

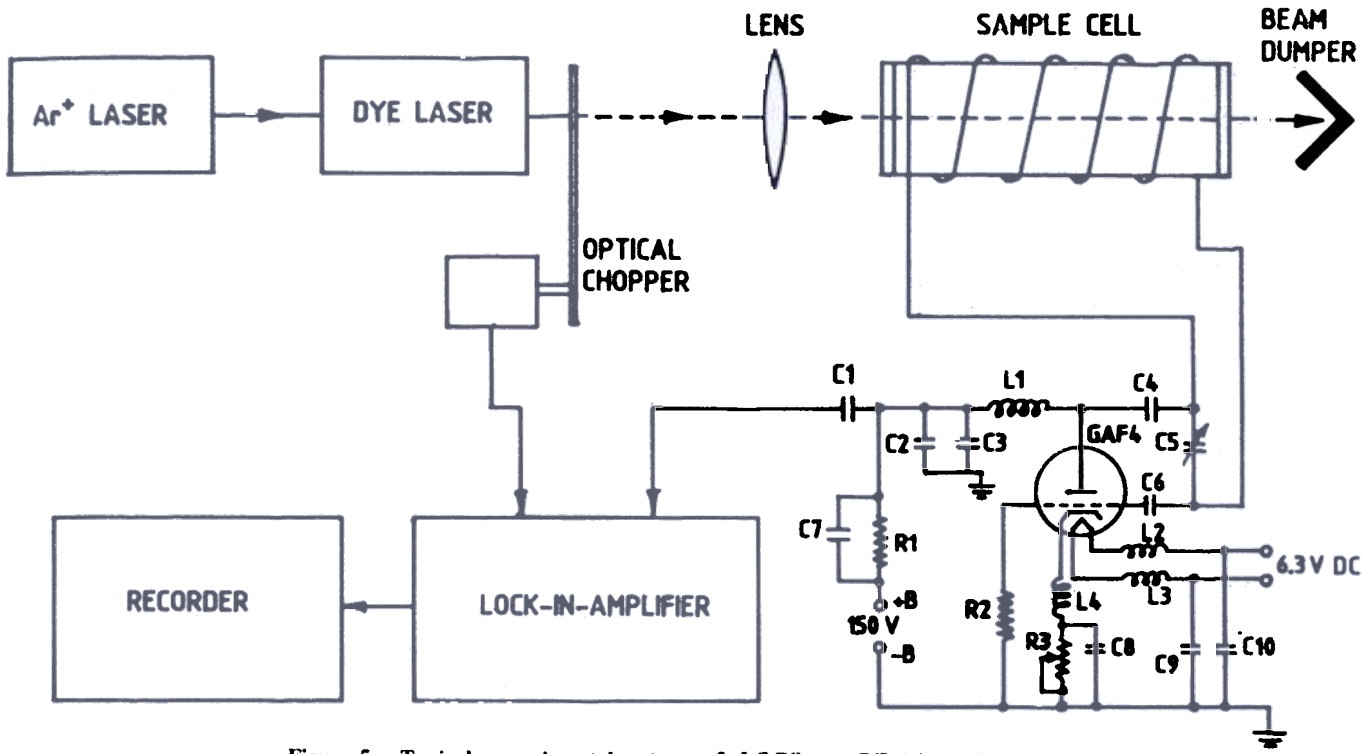

Figure 5. Typical experimental set-up of LOGS on RF-driven discharge.

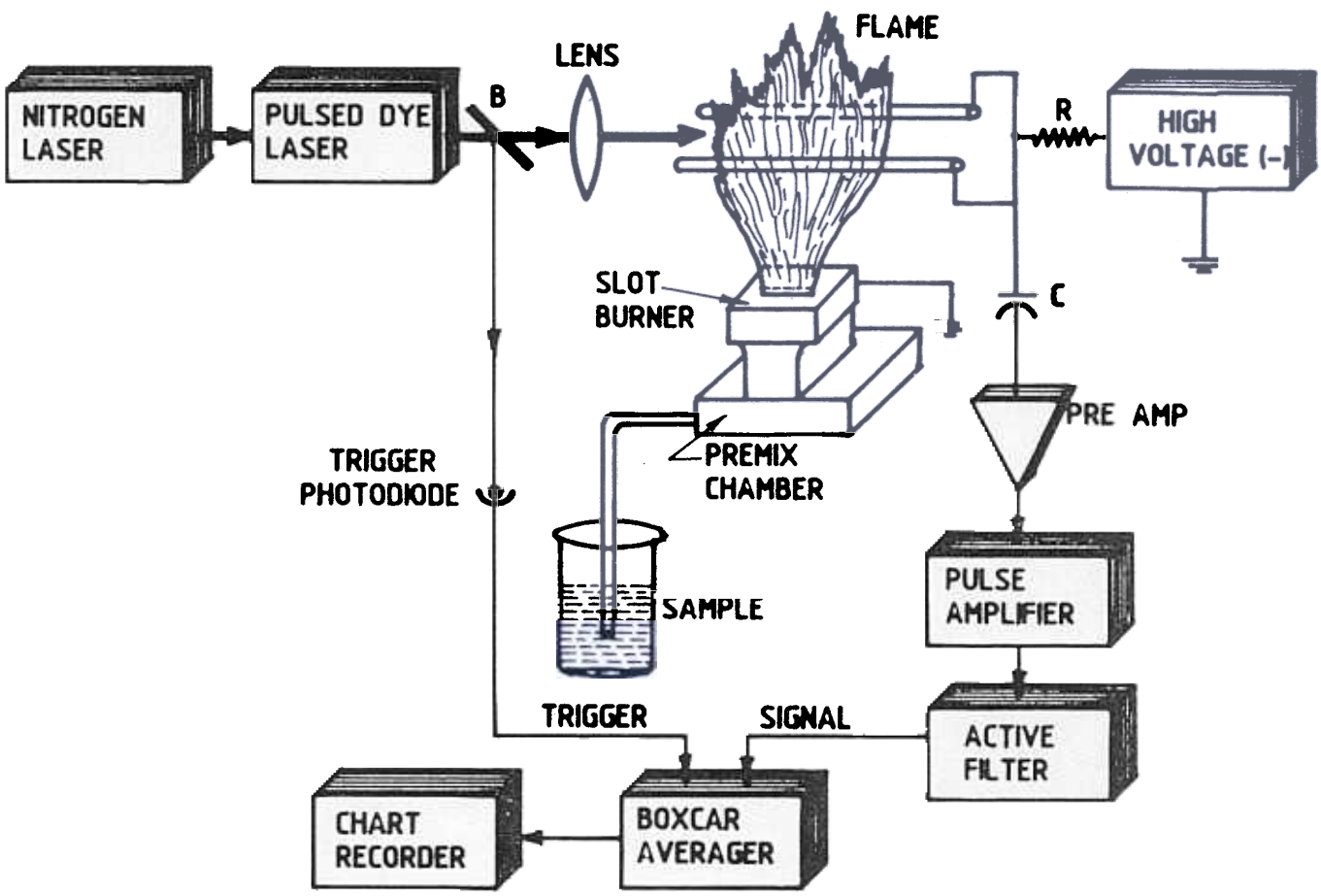

Figure 6. Typical experimental arrangement for pulsed-laser optogalvanic spectroscopy on analytical flames.

3.5 Thermionic Detection

Thermionic diode which works in the space-charge limited mode is an extremely sensitive detector for positive ions having a large dynamic range. There are many different designs of thermionic diodes but the simplest one, in general, consists of a cylindrical anode with an axially mounted cathode filament[15]. The filament is heated directly by a DC current. With an alkali-activated filament, an intense thermionic emission of electrons is achieved. The formation of electron cloud around the cathode limits further increase of current of the diode. Normally no bias is applied to the diode working in the space-charge limited mode.

If a diode is filled with a gas or metal vapour at low pressure and irradiated with a laser light, ions are created inside the diode by resonant photoionization of atoms or molecules. The ions produced at some distance from the hot wire move slowly towards the virtual cathode where they are trapped in the negative space charge potential for considerable long times (> 25 ms). This causes a partial electron space neutralisation which, in turn, enhances a supplemental electron current in the diode at a stupendous rate of $10^4 - 10^6$ electrons/ion internal amplification. A remarkable ion detection sensitivity of the order 1-100 ions/s is thus achieved in this method. The current signals measured using this technique were found to be linear at least over four orders of magnitude. An experimental set-up for pulsed thermionic detection is shown in Fig. 7.

4. APPLICATIONS OF LASER OPTOGALVANIC DETECTION TECHNIQUE

LOGS can have numerous practical applications owing to its many intrinsic advantages over other optical

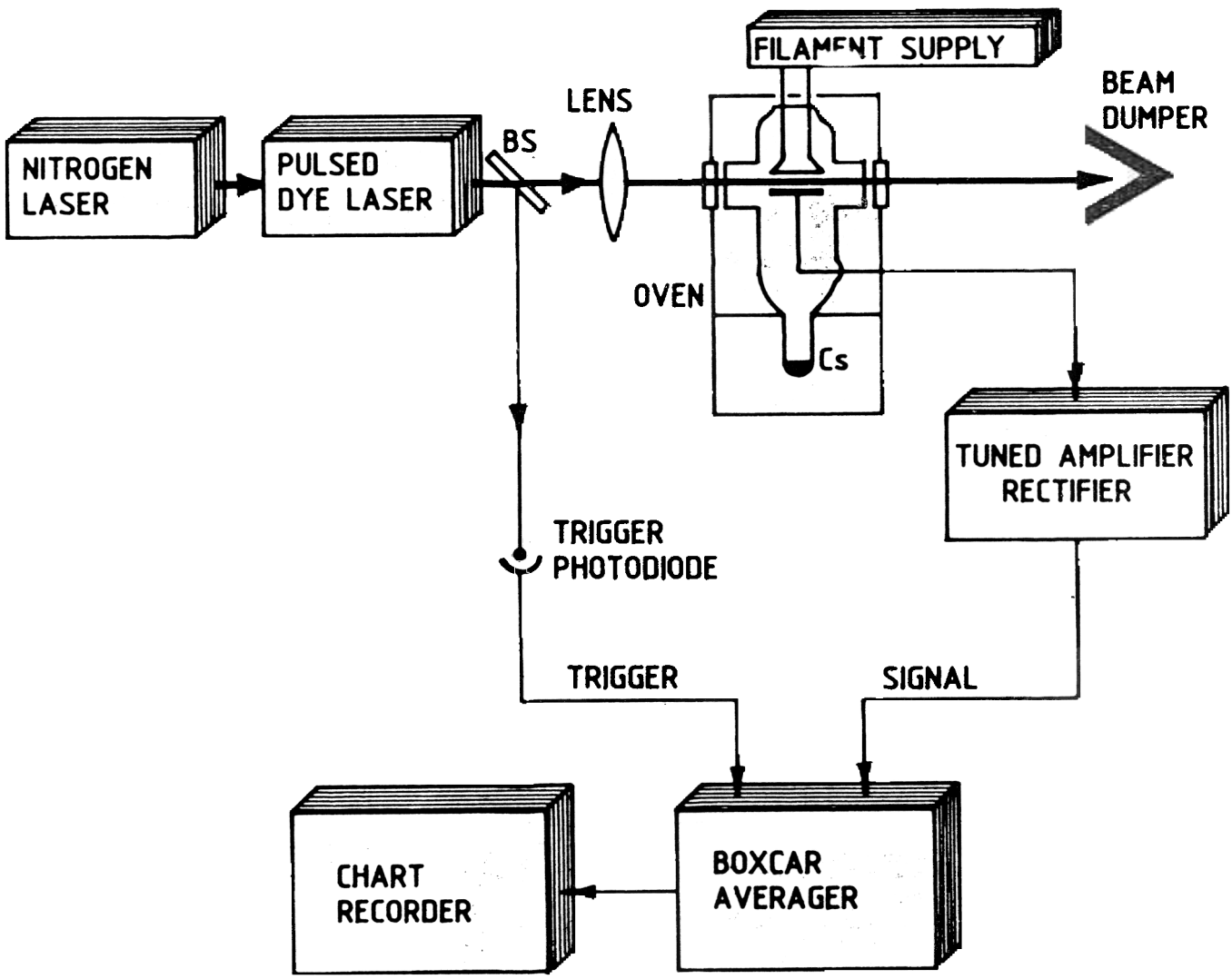

Figure 7. An experimental set-up for thermionic detection of atomic cesium.

detection techniques. Only the applications which are widely studied and technically feasible are discussed.

4.1 Wavelength Calibration

Optogalvanic spectra of elements like argon, neon, uranium and thorium have a number of strong spectral lines which are well spread over the visible and near-IR regions. These spectral lines are not only classified unambiguously but their relative intensities in emission are tabulated by many authors, including the NBS[16,17]. The spectrum of unknown sample is directly calibrated to a high degree of accuracy (10^{-4}nm) by simultaneously recording the laser-induced optogalvanic spectrum of any one of the above-mentioned elements[12]. In Fig. 8 the fluorescence spectrum of Rhodamine 6G dye from 565 nm to 645 nm is provided a direct wavelength calibration by the broadband optogalvanic spectrum of a helium-neon plasma tube.

LOGS can also be used to determine the bandwidths of multimode lasers very accurately. Since the linewidths of the thermalised discharge species are relatively small, the bandwidth of an exciting broad band laser is readily derived from the recorded optogalvanic profiles. On the other hand, if the bandwidth of the exciting laser is narrower than the Doppler broadened linewidths of the atomic/molecular transitions, the individual optogalvanic line profiles precisely reveal the linewidths of the atomic/molecular transitions. Eventhough the broadening at the atomic transitions in discharges are due to many dissipative processes, it is mainly limited by the Doppler broadening alone in most situations. For example, the linewidth of a neon transition at 588.2 nm in a hollow cathode discharge lamp is estimated to be 0.004 nm at a thermalised temperature of 1800 K. Using the similar experimental set-up as shown in Fig. 1, the optogalvanic signal of the sample species can be recorded to estimate the linewidth or bandwidth of the laser by measuring the full width at half maximum of the recorded optogalvanic line profile[18]. Discharge pressures and translational temperature of the species can perhaps be derived from similar studies using high-resolution LOGS with the help of single-frequency tunable lasers.

4.2 Trace Analysis and Concentration Measurement

As an ultrasensitive detection technique, LOGS can be a powerful tool in trace element detection. It can be verified from Fig. 9 that a trace element, potassium present as a contamination in sodium (99.999 per cent pure) is detected without any ambiguity. LOGS is best suited for trace element detection in analytical flames down to 0.01 ppb level[19]. Concentrations as small as picogram per mL (i.e., 10^5 atoms/cm^3) are routinely detected in alkali elements and the observed signals are generally linear in concentration over four orders of magnitude. The experimental arrangements used for this purpose are exactly similar to the set-up shown in Fig 6. Solutions of the metallic samples are generally aspirated into the flames where they are vapourised and decomposed into atomic form. Even though the air-acetylene flames are generally used for this purpose, the acetylene flame with nitrous oxide as oxidant will be the most practical in terms of good atomisation, stability and freedom from inter-element interference effects. With the help of stepwise laser enhanced

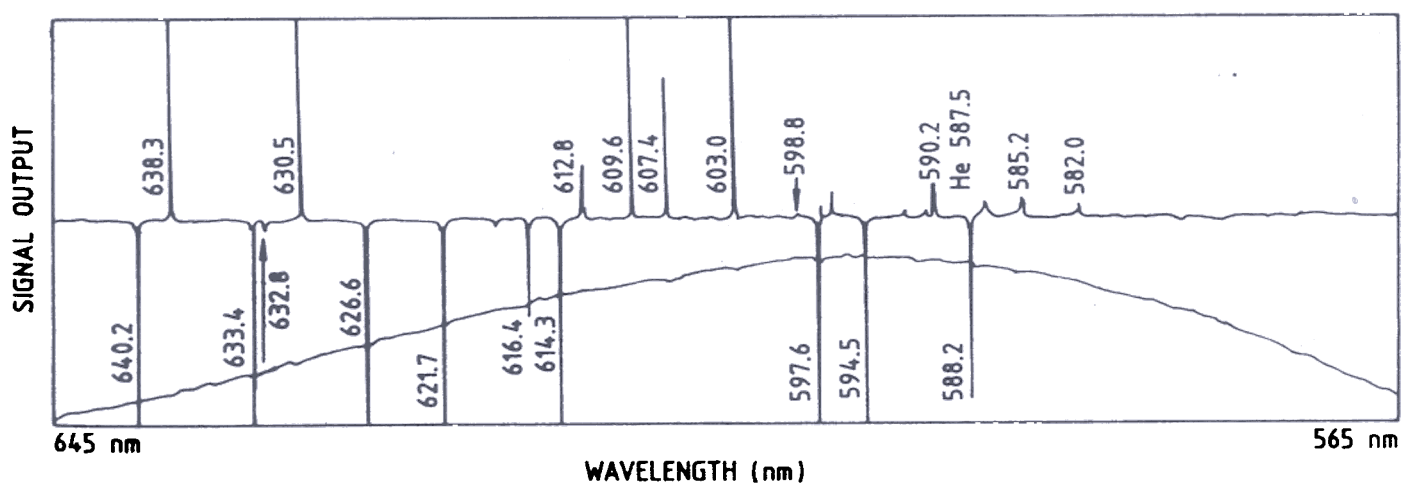

Figure 8. Wavelength calibration of the fluorescence spectrum of Rhodamine 6G dye using broadband optogalvanic spectrum of helium-neon discharge.

ionisation, a further improvement in sensitivity and selectivity is achieved.

Using thermionic diode, scarcely available traces of the order 1-100 atoms/s are easily detected due to their one-to-one conversion into positive ions. Isotope-selective trace-element detection down to femtogram limits is practically achievable in thermionic detection by investigating the high-lying levels of the trace atoms.

4.3 Material Characterisation

It is important to know the purity of materials and composition of alloys to a very high degree of accuracy as they are very important in the manufacture of hi-tech products and in aerospace industries. Since LOGS is a unique technique by which almost all the elements in the periodic table can be studied in one form or the other, it can be a very convenient method to investigate the quality of materials. Solids formed of highly refractive elements can be investigated using this method in hollow cathode discharges in which the materials are vaporised layer by layer by sputtering process[12]. Thus an additional scope for selective analysis of surface layers of materials and determination of elemental composition with depth is offered by this method. Detection limits of 1-100 ppm in alloys are usually possible in hollow-cathode light sources. Materials including metal alloys can also be investigated by this technique through flames by dissolving them in acids and introducing into a slot burner.

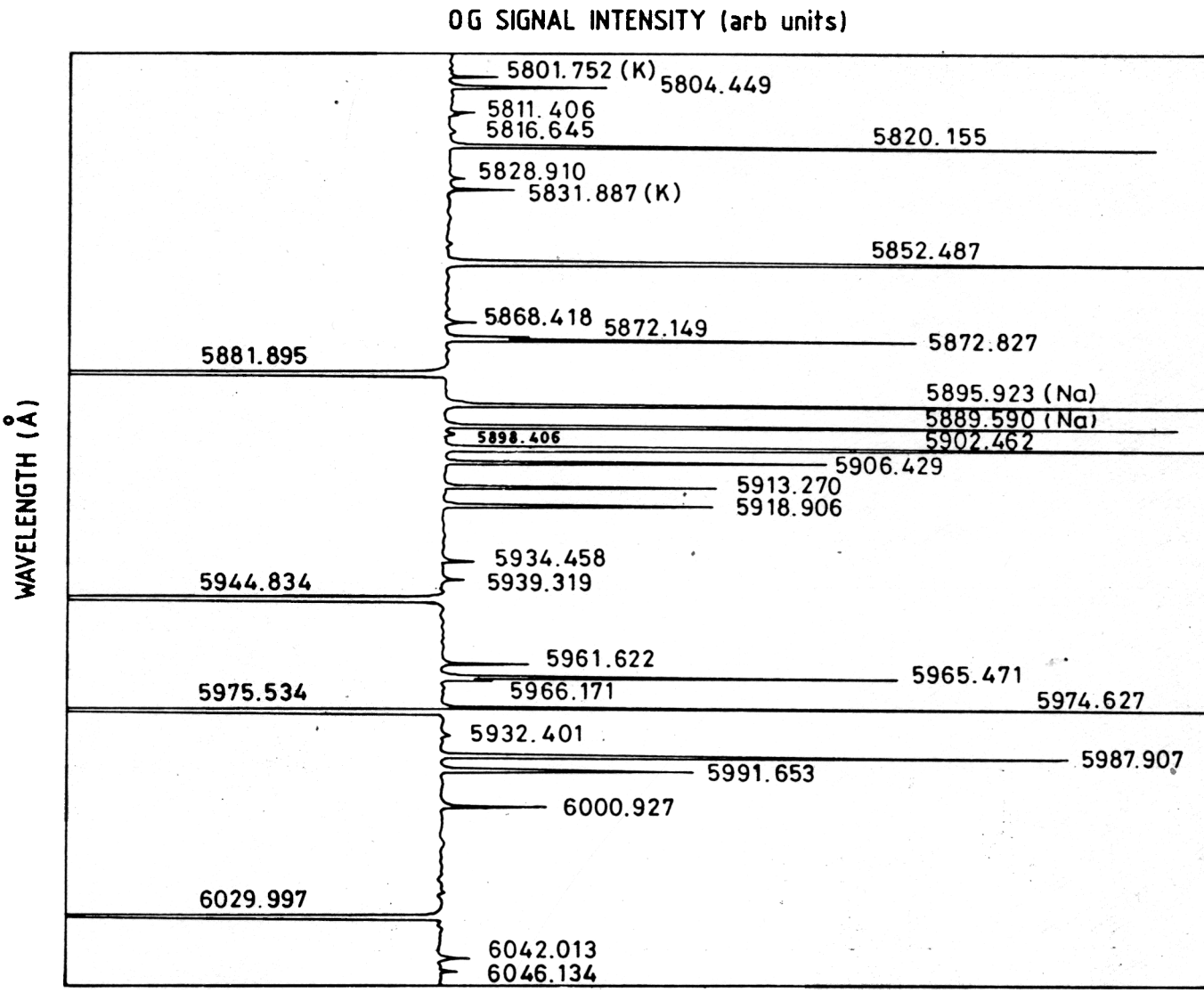

Figure 9. Laser optogalvanic spectrum of sodium-neon hollow cathode lamp. Detection of potassium contamination in pure sodium (99.999 per cent).

4.4 Laser Frequency and Power Stabilisation

Laser optogalvanic signals are used in a number of ways to provide active frequency-stabilisation to all kinds of lasers. The standard technique is based on the impedance change in the discharge as a function of the output power of the excitation laser. Since the frequency drift or modulation in frequency is caused by a change in the effective length of a laser cavity, the frequency of a laser can be stabilised by correcting the cavity length. The optogalvanic signal which results from a change in the output power of the laser following a change in the frequency, serves as a sensitive error signal. This is processed electronically and fed back normally to a PZT-mounted cavity mirror to correct the cavity length. Based on this technique, the frequency of a dye laser can be locked to the centre of any atomic/molecular transition. The long-term frequency stabilisation of 2×10^{-10} was achieved in a low-pressure CO_2 waveguide laser by locking the laser frequency to a narrow Lamb dip in OG effect[20]. The same technique is used to stabilise the frequency of even high-pressure lasers on any lasing frequency by placing a low-pressure discharge tube inside the laser cavity for Lamb dip optogalvanic detection[21]. A continuous tuning of stabilised frequency over a wide portion of the broadened gain profile is also achieved with a zero offset facility in the feedback loop.

An experimental set-up for stabilisation of oscillation frequency of a *GaAlAs* semiconductor laser is given in Fig. 10. The wavelength of the semiconductor

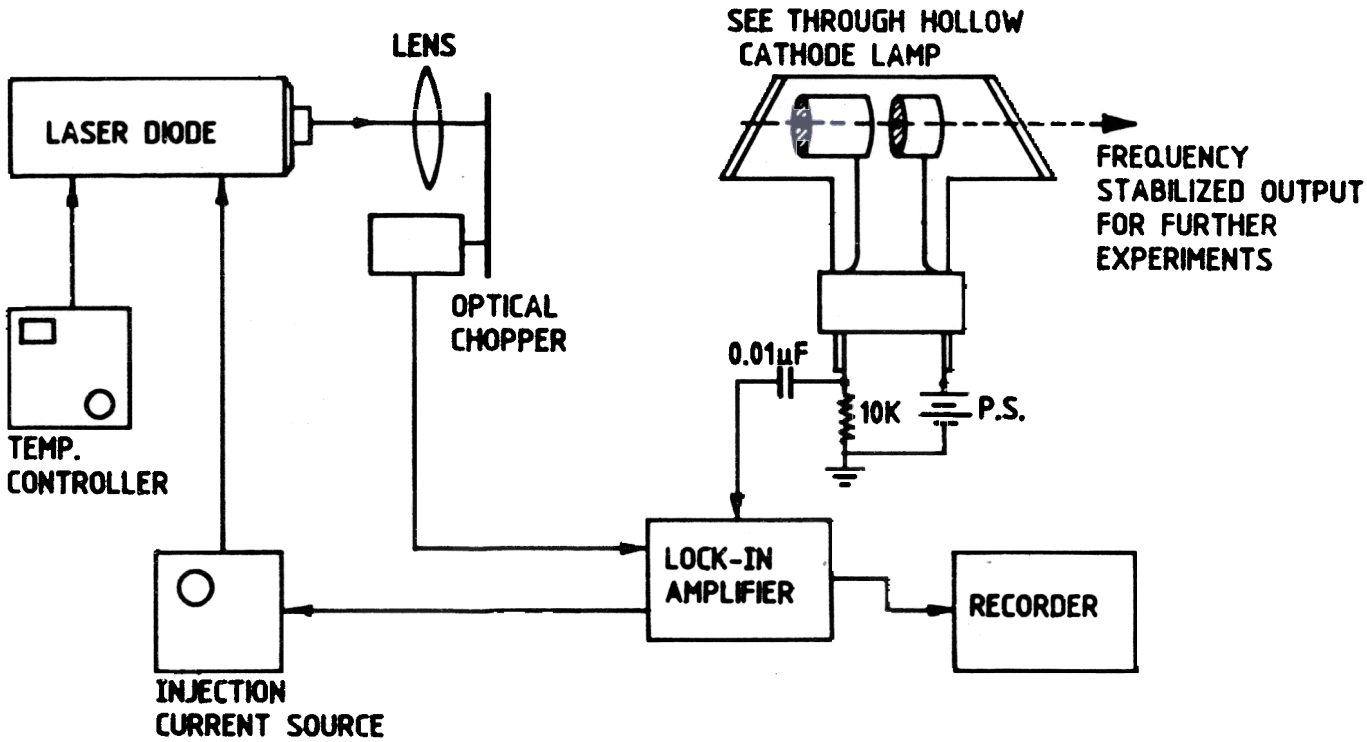

Figure 10. Laser optogalvanic frequency-stabilisation scheme for a semiconductor laser.

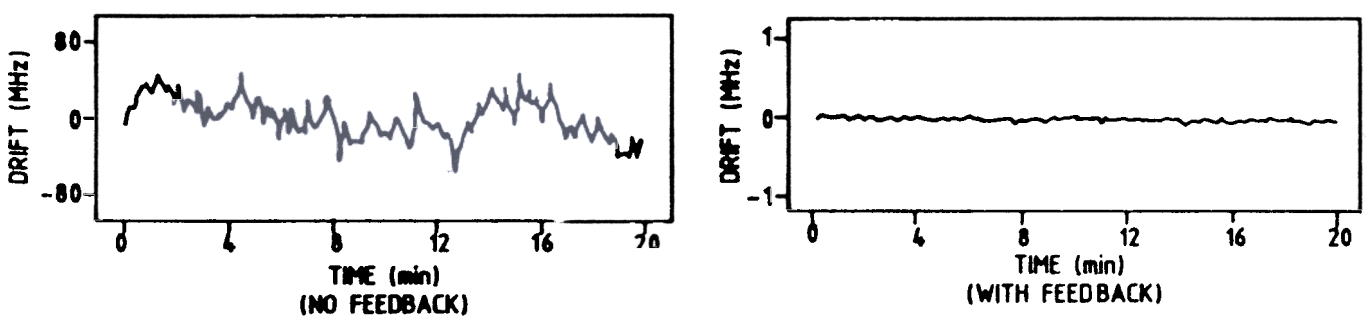

Figure 11. Frequency-stabilised semiconductor laser output

laser is tuned to the resonance of an atomic absorption of UI. When the wavelength of the laser varies, the impedance of the hollow cathode discharge varies. This OG error signal is fed back to the semiconductor laser injection current supply to control the injection current for correction of wavelength. The comparison of stabilised laser output with the unstabilised output is given in Fig. 11.

4.5 Isotope Analysis

To resolve the isotope shifts or hyperfine components of an atomic/molecular energy level, the main spectral broadening contribution from the Doppler effect must be removed by the Doppler-free spectroscopic techniques. LOGS has led to the discovery of some very sensitive new Doppler-free spectroscopic techniques for performing high-resolution spectroscopy. The prominent techniques include intermodulated optogalvanic spectroscopy (IMOGS)[22] and polarisation intermodulation excitation (POLINEX)[23]. In IMOGS, the exciting laser beams are modulated in amplitude while they are modulated in polarisation in POLINEX. But in both the methods, the counter propagating beams when tuned to the centre of an atomic/molecular transition will interact with the atoms/molecules with zero component of velocity (v_z = 0) along the line of beams. In IMOGS, the resolution is limited by the presence of large Gaussian pedestals due to elastic velocity-changing collisions. This problem is completely removed in POLINEX in which the Doppler-free signals arise only from light-oriented atoms which have not been affected by collisional depolarisation.

The typical experimental set-ups of IMOGS and RF-discharge POLINEX are given in Figs. 12 and 13, respectively. In IMOGS, the saturating beams are modulated at frequencies f_1 = 550 Hz and f_2 = 978 Hz and the Doppler-free signals are detected at intermodulated frequency ($f_1 + f_2$). In POLINEX, the laser beams are polarisation-modulated by two spinning linear polarisers at frequencies f_1 = 25 Hz and f_2 = 112 Hz. The narrow Doppler-free signals are detected at intermodulated frequency $2(f_1 + f_2)$. The recorded Doppler-free OG signals of neon are shown in Fig. 14.

4.6 Study of Rydberg Atoms and Molecules

LOGS is best suited for studying the high-lying levels (Rydberg states) corresponding to high principal quantum numbers, say n = 20 and up to n = 500. Low-pressure glow-discharge plasma usually consists of high electron temperatures (10^4 -10^6 K) which ensures

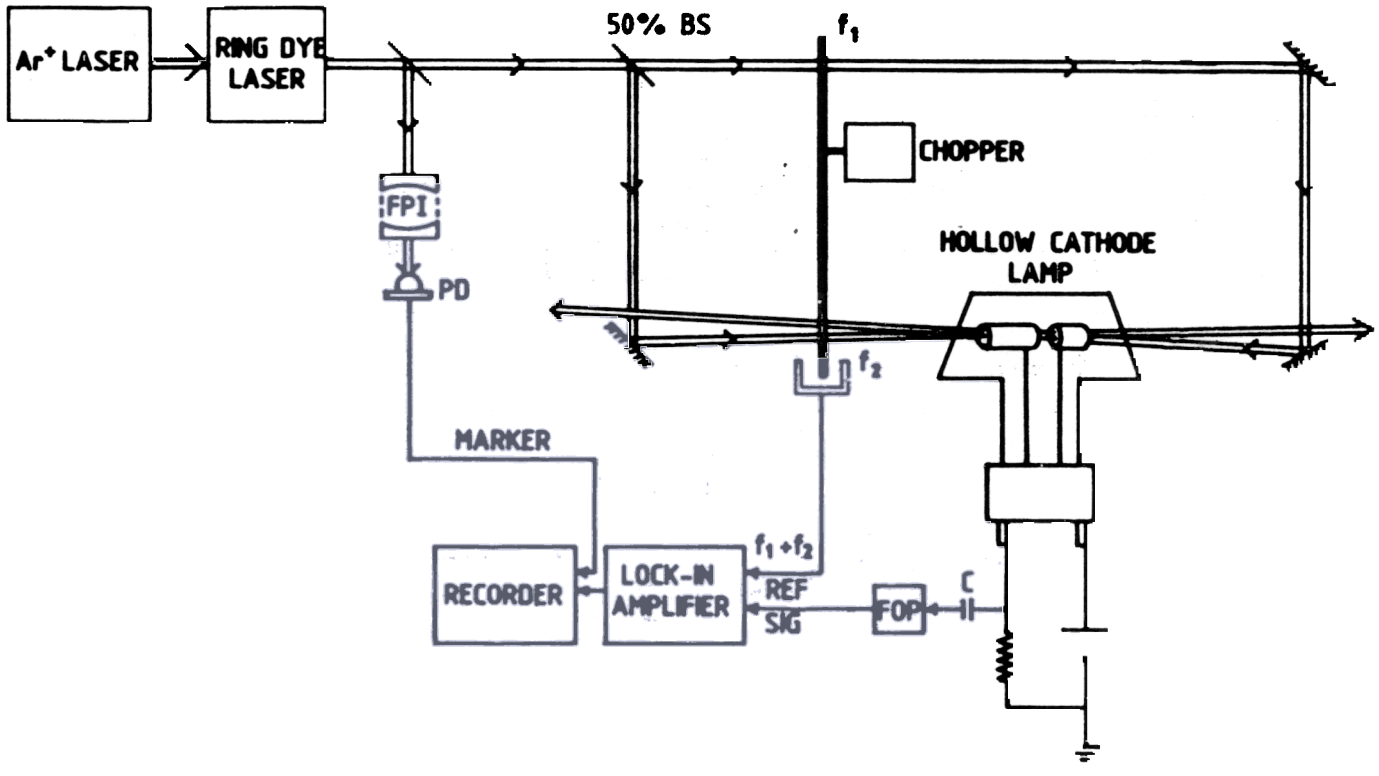

Figure 12. Experimental set-up of IMOGS in a see-through hollow cathode lamp.

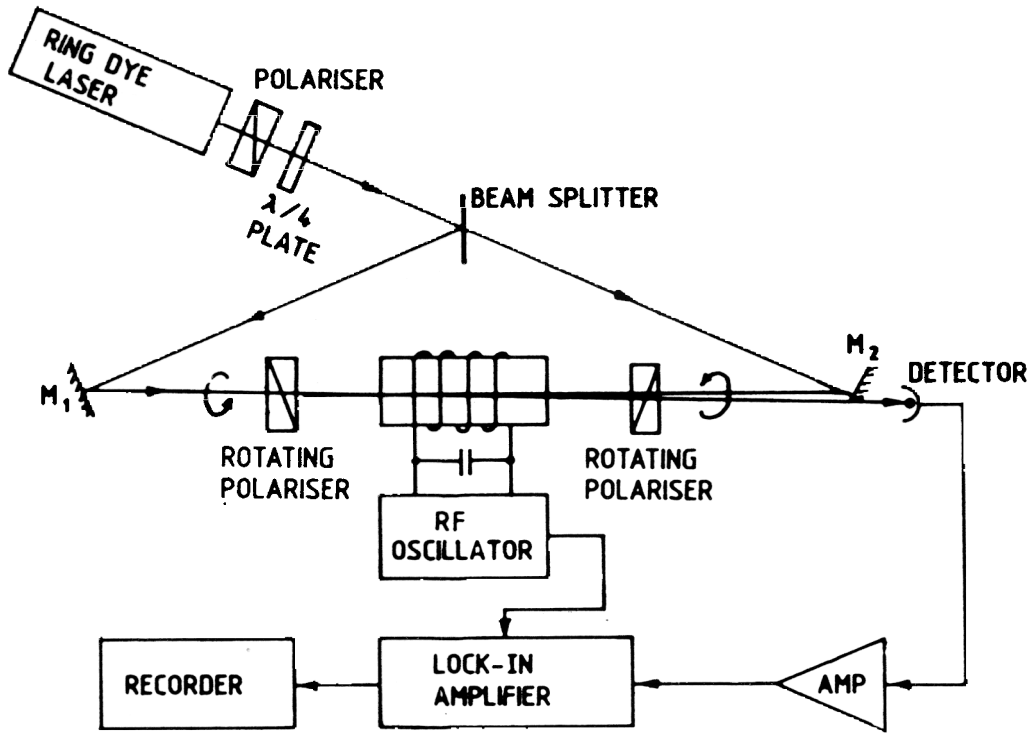

Figure 13. Experimental set-up of POLINEX in RF-discharge.

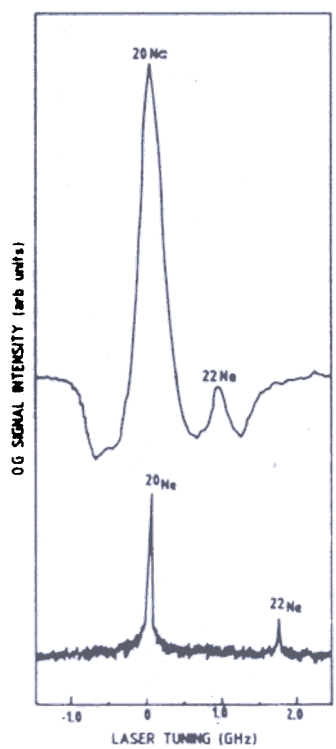

Figure 14. Doppler-free optogalvanic signals of neon for isotope analysis. Frequency scale is different for the two recordings.

a significant population of the excited states, particularly long-lived metastable states. Therefore, the light absorption from excited states in LOGS opens a new field of spectroscopy called Rydberg atom spectroscopy. The recorded hyperfine structure of a high-lying level (n = 25) of sputtered lutetium atoms[23] in a hollow cathode is shown in Fig. 15. Also the thermionic diode is known as an extremely sensitive detector for excited atoms, in particular highly excited Rydberg states. The thermionic detection technique, with its slow response has turned out to be an efficient detector of the Rydberg atoms whose levels have remarkably large radiative lifetimes (milliseconds to seconds) and are fragile to even small electric fields (large Stark effects). On the other hand, the diode has become an outstanding detector in Doppler-free spectroscopy mainly for two-photon absorption. Yet another elegant technique to populate various Rydberg states from the ground state by two-photon excitation via resonant intermediate levels has enabled the researchers[24,25] to study the Rydberg states continuum as close as a few cm^{-1} from the ionization limit. A multi-step and multi-photon laser OG scheme can be well utilised for isotope-separation by exciting the atoms selectively up to an autoionization state.

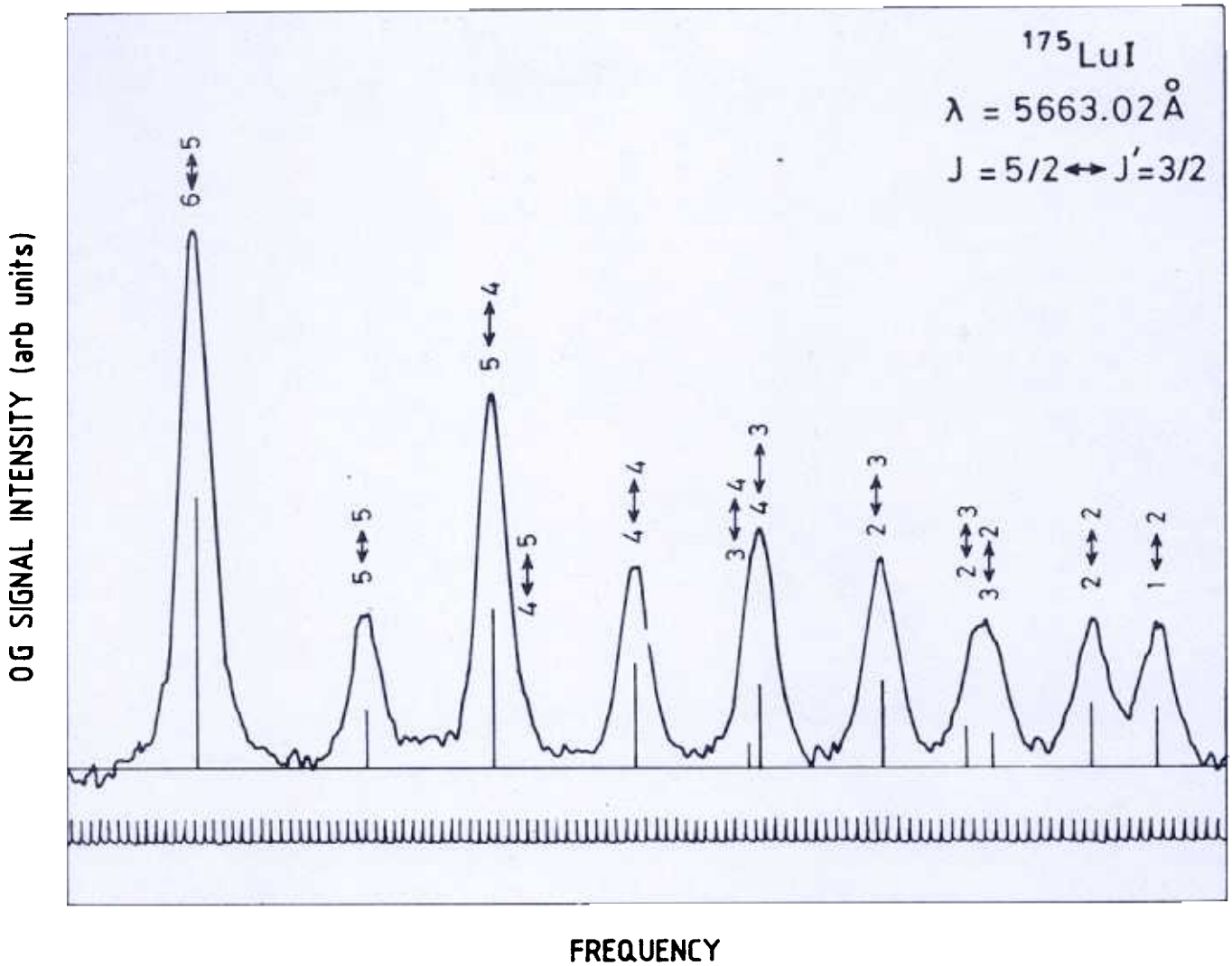

Figure 15. Recorded hyperfine spectrum of *LuI* transition between the high-lying levels $5d^2 6s^4 P_{5/2}$ – $6s^2\ 25p^2 P_{3/2}$ using Doppler-limited LOGS.

4.7 Combustion and Plasma Diagnostics

LOGS using pulsed-laser excitation plays an important role in diagnosing the combustion flames and discharge plasmas. The time-resolved OG signals render possible the investigation of the dynamics of various ionization processes, the possible reaction channels, electron-attachment, detachment, and recombination rates and different transport and relaxation phenomena. The photodetachment OG technique allows the study of negative-ion kinetics which, in turn, helps in determining the electron affinities of atoms or radicals[26].

Experiments based on the state-selective multiphoton OGS can provide the measurement of the relative population of the ground and excited states or population inversions and the translational temperature of the species in the plasma[27]. LOGS can also be employed to determine the ionization cross-sections and relative oscillator strengths of electronically excited states as well as the electron temperature of the discharge.

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