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LASER SPECTROSCOPIC TECHNIQUES FOR TRACE ANALYSIS

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Abstract - The availability of tunable lasers has greatly enhanced the potentiality of laser spectroscopic techniques for trace analysis. Some of these techniques will be briefly reviewed. A high intensity laser beam, with its intrinsic monochromatic character, is an exceptionally useful aid for the study of the interaction of radiation with matter with high selectivity. Laser Resonance Fluorescence (LRF), Resonance Ionisation Spectroscopy (RIS), Selective Excitation of Probe Ion Luminescence (SEPIL), particularly in the case of rare earth ions, are some of the methods which have been used in detecting 10^5- 10^2 atoms/cm^3. Other techniques include use of semiconductor diode lasers (SDL) and Opto-Acoustic Spectroscopic (OAS) methods. Tunable diode laser heterodyne spectroscopy also provides extremely sensitive methods of detection, e. g. ozone in the atmosphere. Availability of high power tunable lasers and refinements in the acoustic detection by extremely sensitive miniature microphones have enabled Spin-Flip Raman Spectroscopy (SFR) and Opto-Acoustic Spectroscopy (OAS) to achieve parts per billion detection capabilities.

INTRODUCTION

The development of tunable lasers has provided extremely sensitive detection of atoms far superior to that normally achieved by conventional methods of analysis. The following methods which have greatly enhanced the potentiality of laser spectroscopic analytical techniques, will be briefly reviewed.

SELECTIVE EXCITATION OF PROBE ION LUMINESCENCE (SEPIL) : RARE EARTHS

In this technique[1] intense fluorescence is excited from lanthanide ions by a pulsed, narrow bandwidth, tunable dye laser. The $4f^n$ electron energy level configuration is different for each lanthanide ion. Hence it is possible to excite each lanthanide selectively in the presence of other lanthanides.

A single crystallographic site for each rare earth ion (site G1) is found to dominate the spectra under proper ignition conditions of the calcium fluoride (containing rare earths). Initially this method was applied for the analysis of Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er and Tm[2]. Subsequently by employing, what is known as the method of associative clustering with a fluorescent probe, the remaining rare earths La, Ce, Gd and Lu could also be determined[3].

The 4f electron solid-state luminescence of lanthanides coprecipitated quantitatively in CaF_2, is excited by a tunable dye laser. Selective excitation of different crystallographic sites of the same rare earth ion is possible because the rare earhts have very narrow energy levels when doped into ordered crystalline media. The intensity of a fluorescent line in the G1 site for each lanthanide is proportional to the concentration of the rare earth. Depending on the temperature at which the precipitate is ignited one or all the four sites, G1, G2, G3 and G4 are observed[4]. When the precipitate is ignited at 600°C, it would show only G1 site while at 1000°C, it would show all the four sites. Since G1 site is the most intense one, some transitions in this site are given in Table 1. The experimental scheme for the technique

for Pr^{3+} is shown in Fig. 1.

TABLE 1. Selected G1 site transitions in order of intensity for $CaF_2:Ln^{3+}$

RE ion	Excitation transition	Excitation λ (Å)	Fluorescence transition	Fluorescence λ (Å)	Relative* intensity
Pr^{3+}	$^3H_4 \longrightarrow {}^3P_O$	4758	$^3P_O \longrightarrow {}^3H_4$	4962.1	2.9
Pr^{3+}	$^3H_4 \longrightarrow {}^3P_1$	4717.9	$^3P_O \longrightarrow {}^3H_4$	4962.1	1.6
Nd^{3+}	$^4I_{9/2} \longrightarrow {}^2G_{7/2}$	5805.9	$^4F_{3/2} \longrightarrow {}^4I_{9/2}$	8697.4	0.7
Sm^{3+}	$^6H_{5/2} \longrightarrow {}^4I_{9/2}$	5054.9	$^4G_{5/2} \longrightarrow {}^6H_{7/2}$	6040.9	0.17
Sm^{3+}	$^6H_{5/2} \longrightarrow {}^4G_{5/2}$	5711.2	$^4G_{5/2} \longrightarrow {}^6H_{7/2}$	6040.9	0.17

*Relative intensity is with reference to the Er^{3+} $^4I_{15/2} \longrightarrow {}^4F_{5/2}$ excitation and $^4S_{3/2} \longrightarrow {}^4I_{15/2}$ fluorescence transition.

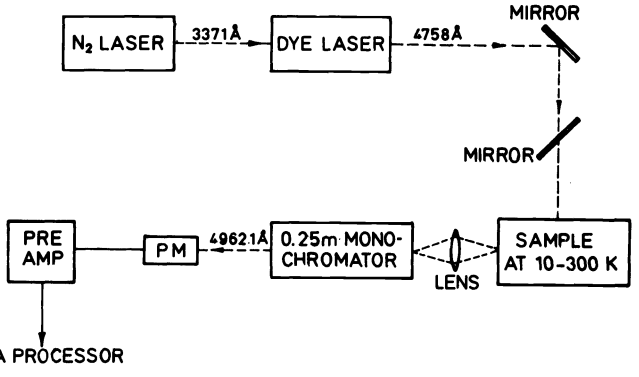
The detection limits of SEPIL compare favourably and perhaps are even better than those obtained by neutron activation analysis which is a widely employed technique for ultra trace analysis. Some of the detection limits obtained in SEPIL are given in Table 2.

TABLE 2. Comparison of detection limits for SEPIL and NAA[1-2]

RE ion	SEPIL ng/ml	NAA
Ce^{3+}	0.004	5
Pr^{3+}	0.0024	0.1
Nd^{3+}	0.45	5
Sm^{3+}	0.063	0.03
Eu^{3+}	0.0004	0.0015
Gd^{3+}	0.046	1

Fig. 1

Experimental set up for SEPIL (Schematic)



LASER RESONANCE FLUORESCENCE (LRF) AND RESONANCE IONISATION SPECTROSCOPY (RIS)

A two-step or multi-step excitation/ionisation is one of the most universal method for selective interaction between laser radiation and atoms/molecules[5-8]. In principle, a laser radiation of frequency ν_1 is absorbed by atoms selectively and transitions to excited state take place. The excited atoms give rise to resonance fluorescence which can be detected. Using such a Laser Resonance Fluorescence (LRF) method, Fairband and She succeeded in detecting 100 atoms/cm^3 of sodium in an evacuated cell[9].

Alternatively, a multi-step photon absorption process can take place, in which the final state is the ionisation continuum of an atom. This is known as Resonance Ionisation Spectroscopy (RIS). The final stage can be saturated with the available

pulsed lasers, so that one electron can be removed from each excited atom of the select type. Using this method nearly all the elements can be detected with commercially available lasers.

Other techniques include use of semi-conductor Diode Lasers (SDL) and Opto-Acoustic methods. Tunable diode laser heterodyne spectroscopy also provides extremely sensitive method of detection, e.g. ozone in the atmosphere[10].

OPTO-ACOUSTIC SPECTROSCOPY (OAS)

Opto-acoustic spectroscopy consists of the measurement of optical absorption by the acoustic signal generated as a result of the absorption and relaxation. The first opto-acoustic experiment was carried out by Bell and others[11-13], when they showed that radiation absorption in a gas produced pressure fluctuations which could be measured by the resultant acoustic signal. The technique has since then been used extensively under the name of non-dispersive infrared (NDIR) technique for process control and trace analysis.

The technique has now achieved new capabilities[14-16] hitherto unrealised, mainly for two reasons; the first is the availability of high power tunable lasers and the second the refinements in detection made possible by extremely sensitive miniature microphones.

In a conventional absorption technique, small amounts of absorption can be measured only with great difficulty, since this involves measurement of a small change in a large background signal. In opto-acoustic technique, the signal produced is measured against a zero background, and the technique thus resembles fluorescence in its mechanism and sensitivity. The high monochromaticity, power and collimation of lasers make them ideal for opto-acoustic spectroscopy, since these properties allow high selectivity, large signal and micro sampling routinely.

The experimental set-up for the technique is rather simple. A modulated (30-3000 Hz) beam of infrared laser radiation is directed through the gas sample which is enclosed in a cell. The energy absorbed by the gas causes its temperature and hence the pressure to rise. This would give rise to periodic fluctuations due to modulation of the beam and the pressure change is detected by an electret microphone which is a quite sensitive acoustic detector.

The electrical signal from the microphone is proportional to the laser power and the gas absorption strength. Therefore the limitation for the sensitivity of the technique lies mainly in the absorption strength as lasers with a wide range of powers are available. If the laser frequency exactly coincides with the most intense transition of the molecular system under study, the sensitivity will be extremely high. At times when the matching is not exact, one can employ a broad band frequency tunable laser and Stark tuning[17] to achieve exact coincidence.

An enhancement in sensitivity has also been achieved by chopping the incident radiation at a frequency equal to a natural resonant frequency of the sample chamber. The resonant frequency depends on the dimensions of the chamber and speed of sound in the sample gas in the chamber. If the resonance is established, each successive pulse contributes to a standing acoustic wave within the chamber. This enhances the sensitivity by two orders of magnitude or more.

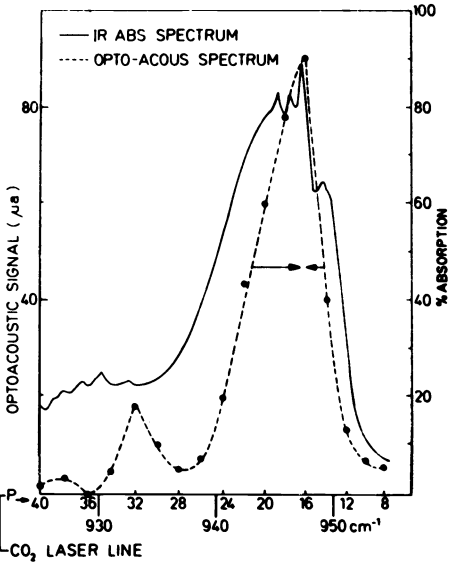
There have been many publications[16-18] in the area of opto-acoustic spectroscopy providing exact coincidences between CO/CO_2 laser lines and absorption lines of many compounds such as ammonia, isotopic species of H_2O and NO, organic compounds like methane, ethylene, methanol, benzene, etc. The measurement of these compounds have importance in atmospheric studies and other areas. Monitoring of HDO and D_2O may be of interest for the control of leaks in atomic reactors. Some of the data on coincident frequencies and sensitivities compiled from the literature have been tabulated in Table 3.

TABLE 3. Optoacoustic detection data and laser lines

Analyte	Laser	Laser line wavelength in microns	Sensitivity
NH_3	CO	6.1493	0.4 ppb
C_6H_6	CO_2	9.6392	3.0 ppb
C_2H_4	CO_2	10.5321	0.2 ppb
NH_3	CO_2	10.349	2.9 ppb
H_2O	CO	5.35298	4.2 ppm
HDO	CO	6.00939	42.0 ppm
D_2O	CO_2	9.6575	0.1 ppm
^{14}NO	CO	5.30695	2.0 ppm
^{15}NO	CO	5.40275	0.19 ppm

Fig.2

Optoacoustic Spectrum
(0.5 torr SF_6 in N_2)



Recently, Patel and Kerl[19] have used a detector with 6 miniature microphones. Using 100 mW from a Spin-flip Raman laser they have detected NO at concentration levels of 10^7 molecules/cc. With such high sensitivity, spectra can now be obtained for molecular species such as excited state molecules, free radicals and clusters which may be present in extremely small concentrations.

OPTO-ACOUSTIC SPECTROSCOPY FOR STUDY OF LASER INDUCED REACTIONS

Very often, in laser induced reactions in molecules, it is essential to know the precise frequency dependence of absorption of laser radiation, for extremely small amounts of samples. This is almost impossible by conventional absorption methods since we have to measure extremely small change in a very large amount of energy in the laser beam. The opto-acoustic method is very well-suited for this purpose. We have obtained[20] the opto-acoustic spectrum of SF_6 (Fig. 2) with a CO_2 laser. The opto-acoustic system and the CO_2 laser were fabricated in our laboratories.

The opto-acoustic spectrum was taken with a few ml of nitrogen having SF_6 at a partial pressure of 0.5 torr. What is to be noted is the clear opto-acoustic signal at the P-32 branch of the CO_2 line (Fig. 2) due to 30 vpm of $^{34}SF_6$ in a few ml of the mixture. The I.R. spectrum, using about 300 ml of the pure SF_6 gas, on the other hand, shows a poor signal at the same frequency. That smaller samples can be studied by OAS, is also clear.

PHOTO-ACOUSTIC RAMAN SPECTROSCOPY (PARS)

This is a new non-linear spectroscopic technique which combines the principle of coherent Raman spectroscopy with the high sensitivity of opto-acoustic detection. Stimulated Raman scattering is used to produce internal excitations (vibrational and rotational) in the gas sample. The energy thus deposited, relaxes giving the acoustic signal. In the actual experiment a cw argon ion laser at 514.5 nm was used as the pump beam ω_p. A second tunable dye laser was then used as the Stokes beam ω_s. Whenever $\omega_p - \omega_s$ coincides with a vibration-rotation energy level, stimulated scattering takes place providing vibrational-rotational excitation. Consequent de-excitation gives the opto-acoustic signal. Compared to other non-linear techniques like CARS, no phase matching is required in this method. Similarly non-resonant background interference which is the major drawback of CARS, is avoided here. Finally, the energy of absorption is measured directly, and not the change in energy

as in SRGS.

SPIN-FLIP RAMAN SPECTROSCOPY (SFR)

The spin-flip Raman laser action was first reported by Patel and Shaw[21] in a sample of suitably doped InSb pumped with a 10.6 micron CO_2 laser. The InSb sample consisting of plane parallel surfaces was kept at low temperature in a magnetic field. With a high intensity of the pumped laser radiation, the processes of spontaneous spin-flip Raman scattering from the electrons in InSb in the magnetic field, B, can be made to go over into the region of stimulated SFR scattering, i.e. SFR laser. The SFR laser frequency, ω_s is given by

$$\omega_s = \omega_o - g \mu_B B$$

Where g is the g-value of the electrons in InSb, and μ_B is the Bohr magneton.

In the studies of spontaneous laser scattering from electrons in semi-conductors, stimulated SFR scattering is the most intense where one obtains tunable Raman scattering and narrow line widths. There are two more processes

1) $\omega_s = \omega_o - 2\omega_c$ involving a change in the Landau level quantum number by 2. The energy of input photon is thus changed by approximately $2\omega_c$

2) $\omega_s = \omega_o - \omega_c$ Where Landau level quantum number is changed by 1.

As mentioned earlier, the SFR process involves stimulated Raman scattering of cross-section 10^{23} cm^2 sr^{-1}, line width approximately 1 cm^{-1} and expected Raman gain at 10.6 microns of approximately 10^5 cm. ω^{-1}.

At present there are more than half a dozen SFR lasers using different semiconductor materials like InSb, InAs, HgCdTe and CdS, with different tuning ranges and power outputs. These are used for high resolution spectroscopic studies and for trace level detection of pollutants in the atmosphere and in the stratosphere. Concentrations of NO as small as 10^7 cm^{-3}, using the SFR laser -opto-acoustic spectroscopy technique, have been determined. By lifting the SFR laser optoacoustic spectrometer to an altitude of 28 km (using balloons) it has been possible to measure NO concentration in situ and obtain its diurnal variation.

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