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RAMAN SPECTROSCOPY IN THE ANALYSIS OF FIRE GASES

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Raman Spectroscopy in the Analysis of Fire Gases

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Raman scattering is a possible technique for analysing gas mixtures. In the work here described Raman scattering was used for detection of gases extracted from different model fires, where wood, polymethyl-metachrylate (PMMA) and polystyrene were used as test materials. Raman spectra of gas samples from differently ventilated model fires are presented as well as the variation of O₂, CO₂ and CO concentrations as a function of time with an effective time constant of less than 5 s. The sensitivity of the experimental set-up was estimated to be about 1000 ppm, but suggestions are given how to reach a detection limit of about 1 ppm. The feasibility of the technique and various ways of improving it are briefly discussed.

INTRODUCTION

During the last years there has been a large increase in analytical applications of laser spectroscopical techniques. The energy crisis has stimulated the interest in combustion research and the laser techniques have become very valuable tools for measuring flame temperatures and flame constituents.¹⁻³ The goal for this research is a better understanding of combustion processes, for optimized combustion and minimized formation of different pollutants. Detection of air pollutants in the atmosphere is also feasible with laser techniques⁴ and the technology is approaching an operational status.⁵ The techniques that have attained most attention for analytical use in combustion diagnostics are laser-induced fluorescence (LIF),⁶ Raman scattering⁷ and Coherent Anti-Stokes Raman Scattering (CARS).⁸

With LIF it is possible to measure molecules, e.g. NO, OH, CH₂O, SO₂ and NO₂, which have energy transitions accessible to tunable lasers. With this method it is possible to measure different minor species with a detection limit ~ 0.1 – 10 ppm.² Raman scattering has until now been limited to major species $> \sim 1\%$, but the invention of new and more powerful laser sources seems to lower the detection limit considerably.⁹ CARS is a non-linear process that requires two lasers where at least one must be tunable. The big advantages with CARS are that the whole signal is generated as a coherent beam in the anti-Stokes spectral region. It is thus possible to discriminate against background using a simple aperture for the CARS signal. This technique has successfully been used for temperature measurements in a fired internal combustion engine.¹⁰ However, the CARS technique suffers from being complex and has a detection limit of about 1%, eliminating detection of minor species. In this paper Raman spectroscopy is used for analysis of fire gases. Raman spectra of combustion gases from different burning materials will be presented as well as concentration values for CO, CO₂ and O₂ as a function of time after ignition.

Raman spectroscopy

Raman scattering, first observed in 1928 and named by its discoverer C. V. Raman, was until the invention of the laser a too cumbersome tool for analytical purposes. However, the use of lasers has greatly increased the applicability of the Raman effect for both quantitative and qualitative analyses of liquids and gases.

The Raman effect has been described in several works (e.g. Refs 11–14), and the theory is only briefly described here.

When a sample is irradiated with a laser beam at frequency ν_0 , most scattered light is elastic light, i.e. light at the same frequency as the laser source. The elastically scattered light is caused by particles (Mie-scattering) and molecules (Rayleigh-scattering). In contrast to Mie- and Rayleigh-scattering, the Raman process is an inelastic phenomenon. In a classical picture, it is possible to describe the Raman effect as a coupling of laser light at frequency ν_0 and the internal molecular vibration frequencies ν_R of the different molecules present. This coupling results in side-bands, at frequency $\nu_0 - \nu_R$ called the Stokes component, and at frequency $\nu_0 + \nu_R$ called the anti-Stokes component. Since the internal vibrations are different for different molecules, a frequency separation is caused which enables qualitative analysis.

Examples of Raman shifts for some common gases are shown in Table 1, where also the resulting Raman wavelengths for a laser wavelength of 5145 Å are given.

This classical picture is a simplification of the Raman effect. A quantum mechanical explanation needs to regard the molecular vibrations as quantified with a quantum number $v = 0$ for the ground state and $v = 1$ for the first excited state. An energy level diagram for the Raman process is shown in Fig. 1. Here it is clear that the Stokes-shifted light corresponds to excitation from the ground state, whereas excitation from the first excited vibrational state results in anti-Stokes-shifted light. A quantum mechanical descrip-

Table 1. Raman shifts for some important gases in combustion

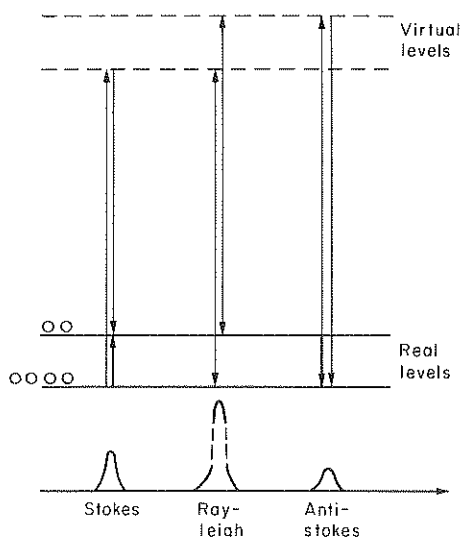
Molecule	Raman shift (cm ⁻¹)	Stokes Raman wavelength [Å] (λ _{Laser} = 5145 Å)
CO ₂ (2ν ₂)	1285	5509
CO ₂ (ν ₁)	1388	5541
O ₂	1556	5593
NO	1877	5695
C ₂ H ₂	1973	5726
CO	2143	5783
N ₂	2331	5846
CH ₄	2915	6053
C ₂ H ₆	2953	6067
H ₂ O	3657	6337
H ₂	4169	6550

tion of the Raman effect explains the intensity differences between the Stokes- and anti-Stokes-shifted light, and since the Boltzmann distribution prevails among the vibrational states, temperature measurements can easily be made just by comparing the Stokes with the anti-Stokes Raman intensities. Figure 1 also shows that Raman scattering is caused via virtual levels, which means that there is no lifetime connected with the Raman process. This is to be compared with laser induced fluorescence where the excited states are real levels.

The number of detected Raman photons N is given by the expression

$$N = \frac{Q\rho\sigma L\Omega\epsilon\eta}{E_\lambda} \quad (1)$$

where Q =energy in the incident laser beam;
 ρ =number density of the molecules in the initial vibrational state;
 σ =differential cross-section per steradian per molecule for the observed molecule;
 L =length of the observed segment of the incident beam;
 Ω =solid angle over which scattered light is collected;
 ϵ =transmission of the receiving optics;
 η =quantum efficiency of the detector;

**Figure 1.** An energy-level diagram for the Raman process.

E_λ =energy of a scattered photon, $E = hc/\lambda$, where h is Planck's constant, c is the speed of light and λ is the wavelength of the scattered photon.

It is evident that absolute measurements of number densities are quite feasible, knowing the constants in Eqn (1). More often however, calibrations of the detection system are made with gases with known concentrations.

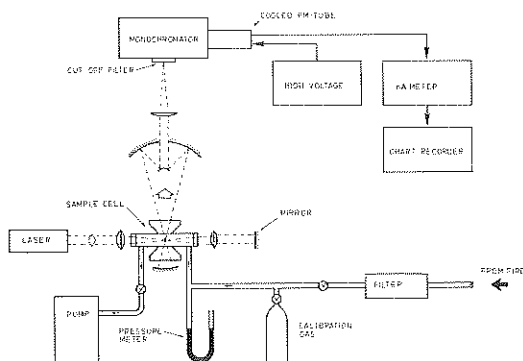
One serious drawback with the Raman effect is that the Raman cross-section σ is very low, about 10^{10} times lower than the cross-section for fluorescence. This limitation makes it important to use high-power lasers and an effective detection system. In order to increase the intensity of the Raman signals several techniques can be used.^{7,9}

EXPERIMENTAL ARRANGEMENT

Since the main purpose of this work is to show the feasibility of the Raman scattering technique, no effort was made to optimize the experimental set-up. As far as possible, equipment already available in the laboratory was used. In particular, the gas sampling and filtering system was quite simple.

Optical system

The experimental set-up used in the Raman experiments is shown in Fig. 2. It is similar to the one used in Ref. 7. We used a Coherent Radiation Ar⁺-laser, with a power of 8 W at 514.5 nm, which was the wavelength used in all experiments. The laser beam was focused inside a specially constructed cell with a lens, $f = 20$ cm. The cell,⁷ shown in Fig. 3, had a volume of 24 cm³ and was equipped with windows made of fused silica in order to minimize laser-induced fluorescence, which frequently causes problems in Raman scattering experiments. The inlet and outlet windows were mounted at Brewster angles so that the reflection losses of the linearly polarized laser beam were negligible. In order to enhance the Raman signals the laser beam was recollimated after the cell with a second lens and reflected back into the cell with a mirror. The Raman scattered light was collected with a Cassegrain telescope placed to fit the f -number of the

**Figure 2.** The experimental set-up for the Raman experiments.

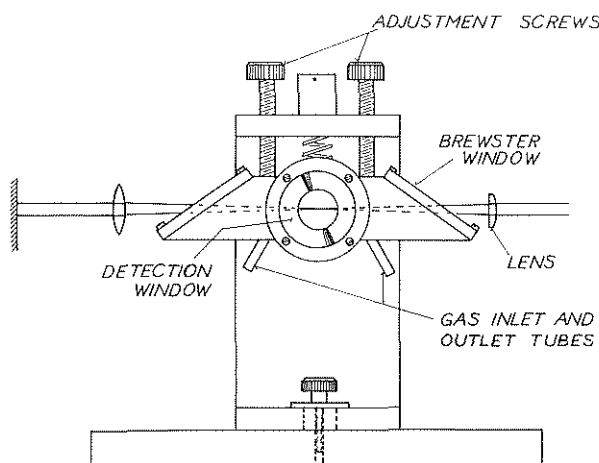


Figure 3. The cell used in the experiments.

monochromator. In order to increase the angle of detection, a spherical mirror was placed on the opposite side of the cell. Before the monochromator entrance slit a cut-off filter (Schott WG550) was placed. This filter blocked all light at the laser wavelength, such as Mie-scattering, Rayleigh-scattering and other types of stray light. The monochromator was a 0.5 m Bausch & Lomb grating instrument with a dispersion of 16 \AA mm^{-1} and an f -number of 4.4. We used a slit-width of 1 mm resulting in a resolution of 16 \AA , which was adequate in our experiments. The Raman light was detected with an EMI 9558 photomultiplier tube.

In order to minimize the dark current, the photomultiplier was placed in a Peltier-cooled housing. The resulting dark current was typically 0.05 nA, whereas the background level was 0.2 nA. The background was mainly due to residual broad-band laser-induced fluorescence from the cell windows and the cut-off filter. The photomultiplier signals were fed to a nanoampere-meter which was connected to a strip-chart recorder. On a second channel a signal from a photodiode, which was detecting the laser power, was recorded in order to be able to compensate for laser power fluctuations. The variations in the laser power were typically less than a few percent.

Combustion system

In all experiments the material was burned on a small tray $80 \times 80 \text{ mm}$ with a 12 mm lip. The materials used were wood (pine), PMMA and polystyrene. The wood fire consisted of nine pieces $15 \times 15 \times 70 \text{ mm}$ forming a three-layer crib. The PMMA and polystyrene was burned as slabs $70 \times 70 \text{ mm}$ with thickness 8 and 6 mm, respectively. For ignition, 6 ml of ethanol was used. The fire, which was in the same room as the measuring equipment, was placed under a small hood connected to a fan for removing the fire gases. In some experiments the fire was placed in a small enclosure, with dimensions $155 \text{ mm} \times 155 \text{ mm}$ and height 240 mm, made from refractory brick. This enclosure had a vertical opening with height 145 mm and a width that could be varied.

The fire gases were sampled using a water-cooled

copper probe, 2 mm in diameter. The gases were pumped through a simple filtering system and then through the scattering cell. The filtering system consisted of glass-wool and cotton for removal of soot, and silica gel for drying the gases. It is possible to measure water if all water is in gaseous form. This could be achieved by using a heated sampling system and scattering cell, but for the reported experiments we avoided this complication.

Measurements and results

Two types of experiments were performed. In one type, gases were sampled from the fire when running close to its maximum intensity and Raman spectra were obtained by sweeping the monochromator. In a second type, the major constituents CO , CO_2 and O_2 were monitored continuously during the time evolution of the fire.

In Fig. 4 Raman spectra for an open-configuration wood fire and for a calibration gas are shown. The fire gas was sampled 140 mm above the center of the tray. The calibration gas contained 2% CO , 5% CO_2 , 1% H_2 and 5% CH_4 with He as buffer gas. The oxygen calibration was made on air. If a calibration gas is not

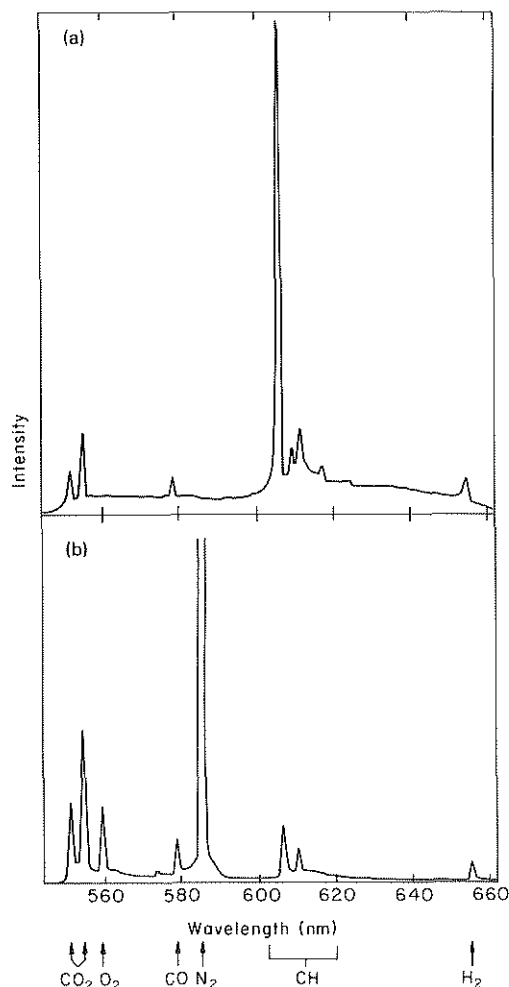


Figure 4. Raman spectra from (a) calibration gas and (b) wood fire.

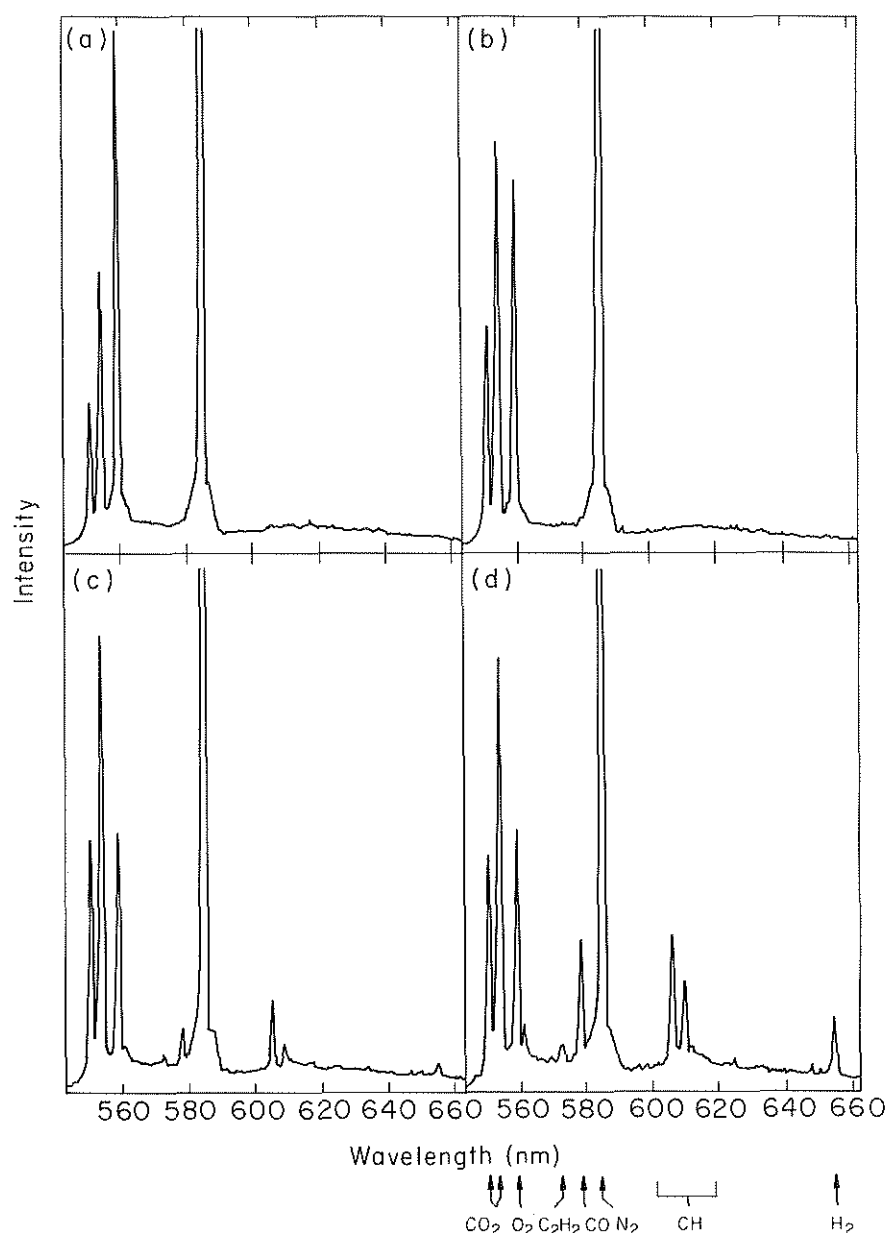


Figure 5. (a–c) Raman spectra of gases extracted from fires at different ventilation conditions; (d) Raman spectrum of gases extracted from a corner position.

available for a specie, the concentration can be calculated using relative Raman cross-sections and correcting for differences in spectral response of the detection system.

Spectra for the wood fire under different ventilation conditions were also recorded. In Fig. 5(a–c) spectra for three opening widths (130 mm, 66 mm and 32 mm) are presented. The gas was sampled at the top of the opening. As can be seen in Fig. 5, reducing the ventilation results in the appearance of more constituents (e.g. CH, CO and H₂). In one experiment, presented in Fig. 5(d), the wood fire was placed in a corner position and the gas sampled only 25 mm above the crib. The concentrations calculated from the spectra in Figs 4 and 5 are listed in Table 2. As expected, the Raman spectrum shown in Fig. 5(d), where the gases were extracted from the corner position, indicates a very fuel-rich gas mixture. It is even

Table 2. Concentrations of different species in a wood fire under different conditions

Molecules	a	b	a	b	c	d
	Reference gas	Wood	130 mm	66 mm	32 mm	corner
CO ₂	5.1	11.5	6.8	10.3	11.6	10.7
O ₂	(20.9) air	4.3	10.6	7.1	4.8	4.8
C ₂ H ₂	—	0.09	—	—	0.06	0.1
CO	2.2	3.5	—	—	1.1	3.6
CH ₄	5.0	0.5	—	—	0.3	0.5
H ₂	1.3	1.0	—	—	0.3	1.4

The first two columns refer to Fig. 4, whereas the other four columns refer to Fig. 5. The concentrations are given in volume percent.

possible to identify C₂H₂¹⁵ at 5726 Å. The concentration of C₂H₂ was estimated using the relative Raman cross-section.¹⁶ The time for recording a spectrum shown in Figs 4 and 5 was about 5 min.

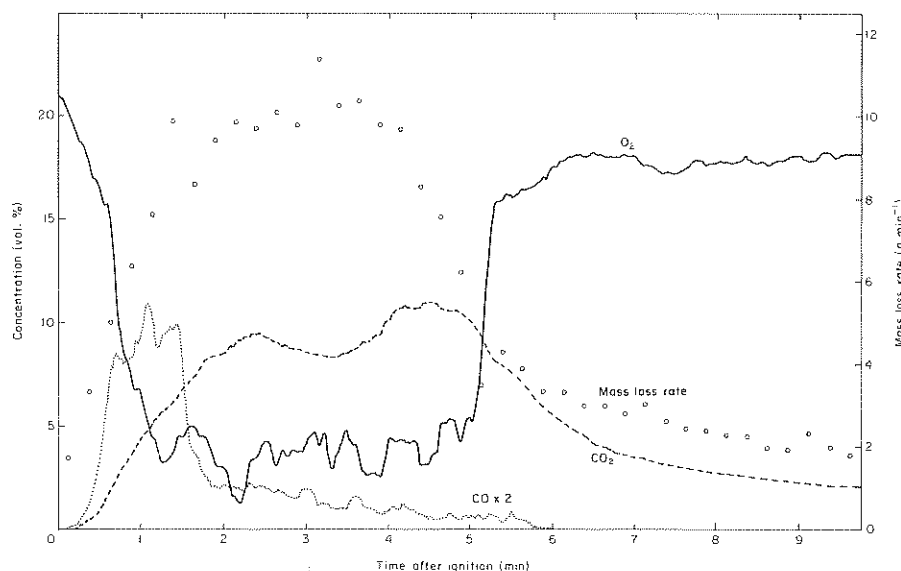


Figure 6. Variation of mass loss rate = $\circ \circ \circ \circ \circ$, O_2 = —, $CO \times 2$ = $\cdots \cdots$, CO_2 = ----, as a function of time after ignition. The burning material was wood.

In the time-resolved measurements, the fires were burning in the open air with a balance registering the mass-loss rate. The monochromator was set on the wavelength of the Raman signal for the specie under investigation and the fire gases were continuously flowing through the scattering cell. The Raman signal was simultaneously registered on a strip-chart recorder. The response time constant in the system was less than 5 s. The concentrations of O_2 , CO and CO_2 are shown in Fig. 6 for the wood fire. The mass-loss rate shown in the Figure was registered in the same experiment as the O_2 recording, but only a small difference in mass-loss rate was recorded for different experiments with the same material. Similar results were obtained when PMMA and polystyrene were burnt, but they will not be presented here. The experiments show that acceptable filtering for particles can be achieved using a quite simple filtering system.

CONCLUSIONS

In this paper we have shown that Raman spectroscopy can be used in the analysis of fire gases, and the technique shows such qualities that it is likely to become a true alternative to conventional techniques.^{17,18} The great advantages with Raman scattering are that almost all molecules may be detected with the same experimental set-up and that problems with overlapping spectra are small for almost all molecules except for hydrocarbons, which all have vibration frequencies around 3000 cm^{-1} , the C-H stretch mode.

In all the experiments, a photomultiplier is used as detector, which means that only one specie could be detected at a time. Especially in the measurements of CO, CO_2 and O_2 as a function of time, it would be favourable to detect *all* species simultaneously. This is possible by using a diode-array detector, which is placed in the focal plane of a spectrometer. The

diode-array detector, which essentially is an electronic photographic plate, enables simultaneous recording of a complete spectrum, which is necessary if proper analysis of all species as a function of time has to be made. If one is interested in only a few species it is possible to use an optical arrangement, which separates the different Raman signals. The Raman signals are then separated by optical filters and detected by different photomultipliers.

In the measurements no explicit effort was made to decrease the detection limit, which was estimated to be about 1%. It is possible to decrease the detection limit by using several passes of the laser beam through the cell, thereby increasing the laser intensity in the focus. Another possibility is to use photon-counting together with a discriminator, which is set to discriminate all pulses but those corresponding to real photons. The lowest concentrations reported with Raman techniques until now were measured using a pulsed excimer laser with extremely high power in the UV region.⁹ Since the Raman cross-section scales as λ^{-4} , an almost nineteen-fold increase in signal is achieved using, e.g., 248 nm as excitation wavelength compared with 514.5 nm for the same laser energy. With the excimer laser it was possible to detect 1 ppm of N_2 in Ar.

In the laboratory at the Department of Physics in Lund there is access to both a diode-array detector and an excimer laser, and the intention is to use this equipment in future experiments for simultaneous detection of minor species.

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