Experiments with Photo Acoustic Spectroscopy and Photo Acoustic Deflection Spectroscopy.

Diploma paper
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Introduction

The photoacoustic (PA) effect have been known for a long time, but its applications have not been developed until recently, by the upcoming of lasers and it has a potential of developing into a good combustion diagnostic technique for minority species.

The Raman-technique is used for detection of majority species and is not sensitive enough for the chemically important radical intermediates at lower concentration. On the other hand the laser induced fluorescense technique (LIF) suffers from collision quenching in a high pressure environment. The photoacoustic spectroscopy technique (PAS) overcomes this disadvantage, making use of the above mentioned quenching.

Theory

The PA effect may be explained quite simply.

A sample of gas (e.g. in a flame) is illuminated by light by such a wavelength that it is absorbed by the gas molecules. The excited molecules can either radiatively decay or lose their energy via collisions. Due to quenching collisions with foreign gas molecules most of the excited molecules decay non-radiatively. Therefore, the energy appears as translational energy of the gas molecules and the subsequent pressure wave may be detected.

Specifically, for a cylinder of radius R and length L, an initial temperature rise

$$\Delta T = \frac{\Delta E}{\rho C_v \pi R^2 L} \quad (1)$$

is created by a laser pulse shorter than the acoustic transit time across the cylinder. The temperature rise is in the order of 1 K and is not perturbing the flame conditions. The pressure in the heated area is simply given by the ideal gas relationship:\(^1\)

$$\Delta P = \frac{\rho R_g \Delta T}{M} \quad (2)$$

and the peak amplitude \(P_c\) of the outgoing pressure wave is half this value. The pressure pulse is followed by a rarefaction wave of substantially equal strength restoring the pressure to the ambient value.

The time separating the positive and negative pulses approximately equals the transit time for the cross-section length of the cylinder at the speed of sound at the actual temperature in the flame\(^2\).

The total acoustic energy in the expanding cylindrical shell is
constant so that the pressure wave decreases as the square root of the distance \( r \) from the centre of the source to the microphone:

\[
P_c = \left( \frac{R}{r} \right)^{1/2} P_c(R)
\]

(3)

or for a spherical shell as a \( r^{-1} \) dependence:

\[
P_c = \left( \frac{R}{r} \right) P_c(R)
\]

(4)

**Experiments**

The purpose of the experiments was to estimate the potential of the PAS technique in a combustion environment.

The combustion environment was in these experiments a flat flame burner (except where else indicated) with an air-methane flame.

Detection of the PA pulse may be carried out in two different ways:

a. By use of a microphone (hereinafter called PAMS (M for microphone))

b. By probing the volume adjacent the pressure source - the pump beam - with another laser beam - the probe beam - and detecting the deflection of the probe beam (hereinafter called PADS (D for deflection)).

The PAMS technique was carried out very easily by just positioning the microphone a little distance from the burner.

The PADS technique was more troublesome in positioning the probe beam very close to the pump beam. Moreover, there were problems in detecting the deflection in itself.
**Temperature measurements**

By measuring the intensities of the various lines in the OH-spectra and dividing by the respective rotational line transition probabilities, one can determine the populations of the various OH-rotational. The slope of a semi-logarithmic Boltzmann plot of these populations should give the OH-rotational temperature.\(^1\)

\[
d \sim A_{nm} e^{-\frac{E_{rot}}{kT}}
\]

\(a\) = acoustic signal  
\(A_{nm}\) = transition probabilities (including degeneracy)  
\(k\) = Boltzmann constant  
\(T\) = temperature

\(E_{rot} = B_v (J+1) = \text{rotational energy}\)  \(\text{(6)}\)

\(B_v = 18,548 \text{ cm}^{-1}\)

**Beam deflection**

The deflection of the probe beam may occur of several different reasons.\(^5\) The beam is deflected by a gradient in the index of refraction. The index of refraction varies with the temperature \((n-1 \sim 1/T)\).\(^6\)

In the case of overlapping pump and probe beams the gradient is produced by the pump beam laser intensity profile which is assumed to be Gaussian.

In the non-overlapping case a thermal gradient results due to geometric spreading of the acoustic pulse produced by the temperature rise. The index of refraction varies with the pressure \((n-1 \sim P)\).\(^5\)

After the initial acoustic pulse propagates another wave due to the relatively slower diffusion of heat. This secondary wave presents another distance dependance than the first acoustic pulse, the diffusion wave getting more diffuse as it propagates outwardly.
**PAMS: Preliminary measurements**

I. The flame was seeded with a small grain of cesium-iodide directly on the burner, in purpose of detecting the signal for the first time. The distance dependence was studied. The signal decreased as $r^{-1}$ implying a spherical pressure wave in agreement with the theory, the pressure source being the comparatively small grain (cf Fig 1).

II. Next step was to use a slot burner normally integral with an apparatus for absorption measurements.

Ordinary salt (NaCl) was solved in water and was sucked in by the gas flow. The laser was tuned to an absorption line of Na at 589 nm. A significant noise level was detected, probably due to the vaporization of the water. The signal to noise ratio ($S/N$) was $\approx 3:1$ (cf. Fig 2a-b). When the microphone was moved the signal moved to the right on the oscilloscope screen and the velocity of sound could be calculated:

$$\Delta r/\Delta t = 6 \text{ cm/} 190 \mu\text{s} = 316 \text{ m/s}$$

(cf. Fig 2a,2c)

The noise decreased with the gas flow and was halved when the suction was removed.

The effect of the laser power was also studied. When the power was doubled the signal was increased by 50%, implying that the signal was saturated. The flame was also completely yellow.

**PAMS: Temperature measurements**

**Apparatus**

With reference to Fig 3, the following apparatus was used.

A Nd:YAG laser pumped a dye laser (Rhodamine 6G). The light was frequency doubled by a KDP crystal (C) and the two frequencies were separated by a Pellin-Brocca prism (P). The UV-light was focused by a $\approx 50 \text{ cm}$ focal-length lens (L), the focal point of which was located in the middle of the flame above the burner (B) and the other beam was directed into a beam dump (D). The burner was mounted on a micrometer calliper, movable in the vertical direction. The microphone (M) was a 4133 Brüel & Kjær and the signal from the microphone was passed through a Brüel & Kjær Frequency Analyzer 2120 and was monitored on an oscilloscope. The oscilloscope was triggered by means of a photo diode (PhD) that responded to the reflected UV-light from a shield (S).

**Measurements**

The signal to noise ratio ($S/N$) was $\approx 100:1$ (cf. Fig 4ab).

The OH concentration in the flame was in the order of 500 ppm.$^7$

Together with the $S/N$ ratio it gives the detection limit for single shot 5 ppm of OH, for a cylinder of length $l = 3 \text{ cm}$ and radius $R = 0.5 \text{ mm}$.

By use of an absorption spectrum table for OH and the PAMS signal four different lines were located by turning the wavelength dial on the
dye laser. One of the selected lines was relatively insensitive to
temperature variations (Q, S) and three more sensitive lines (Q, 8, Q, 10,
Q, 11) were selected. . The lines were blended with other lines.

By use of a power meter the power was kept substantially constant at
= 2.6 mW/pulse at the frequency 10 Hz.

The height of the flame was scanned in steps of 0.5 mm (by turning
the micrometer caliper). The signal was amplified and high pass filtered
(3dB point at 6kHz) through the frequency analyser. The signal was then
measured directly on the oscilloscope screen as the distance between
the positive and negative spikes (cf. Fig 5).

Calculations and results

For the Q, 10 line the acoustic signal was 2.2 Vpp, and subsequently
the amplitude a = 1.1 V. According to Brüel & Kjær the microphone
sensitivity was S = 50 mV/Pa with a correction factor 14dB. The gain in
the frequency analyzer was 50dB, giving a corrected amplification
A = \(10^{\exp((50-14)/20)}\) = 63.1

and the pressure

\[ \text{P} = \frac{a}{(\text{SA})} = 1.1/(63.1 \times 0.05) = 0.35 \text{ Pa} = \text{P}_c(r = 50 \text{mm}). \]

This value might be too low, since the frequency 40 kHz of the PA
signal is near the upper limit of the dynamic range of the microphone.

Since the distance r = 50 mm and the length l = 30 mm through the
flame we approach the spherical case and the formula (4) on page 2
should be used:

\[ \text{P}_c(R) = \text{P}_c(r)r/R = 0.35 \times 50/0.5 = 35 \text{ Pa}. \]

\[ \Delta \text{P} \text{ is twice this value: } \Delta \text{P} = 70 \text{ Pa}. \]

According to formula (2) on page 1 this gives a temperature rise

\[ \Delta T = \Delta \text{P} M/(\rho R^2) = 70 \times 0.029/(0.186 \times 8.31) = 1.3 \text{ K} \]

where

\[ \text{M} = 0.029 \text{ kg/mol} \]
\[ \rho = 0.186 \text{ kg/m}^3 \text{ at 1900 K} \]
\[ R_g = 8.31 \text{ J/molK} \]

and a corresponding amount of absorbed energy according to (1)

\[ \Delta E = \Delta T \rho C_v \pi R^2 l = 1.3 \times 0.186 \times 714 \times \pi \times (0.0005)^2 \times 0.03 = 4.1 \mu \text{J} \]

with

\[ C_v = 714 \text{ J/kgK} \]
\[ R = 0.5 \text{ mm} \]
\[ l = 30 \text{ mm} \]

With a laser pulse energy of 2.7 mJ the absorption is about 0.15%.

The formula (4) on page 3 gives with the adequate J values the
rotational energies. According to the formula (3) on page 3 the
temperature could be determined by dividing the PA amplitudes for the
different heights by the transitional probabilities \(A_{nm}\) and plotting.
against the rotational energies (cf. Fig 6).

<table>
<thead>
<tr>
<th>Line</th>
<th>$A_{nm}^3$</th>
<th>$J$</th>
<th>$E_{rot}/\text{cm}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{15}$</td>
<td>2,2</td>
<td>5,5</td>
<td>563</td>
</tr>
<tr>
<td>$Q_{18}$</td>
<td>67,5</td>
<td>8,5</td>
<td>1498</td>
</tr>
<tr>
<td>$Q_{110}$</td>
<td>84,1</td>
<td>10,5</td>
<td>2240</td>
</tr>
<tr>
<td>$Q_{111}$</td>
<td>92,4</td>
<td>11,5</td>
<td>2666</td>
</tr>
</tbody>
</table>

The transitional probabilities included the degeneracy. The slope of the predicted straight lines give the temperatures for the different heights (cf. Fig 7).

For comparison the temperature was measured with a thermocouple (Pl-Pl 0,87 Rh0,13). The temperature was corrected for the heat transfer from the thermocouple wire:

$$D_0 \rho / \mu_f = 5 \times 10^{-6} \times 0,388 / 97,7 \times 10^{-6} = 0,20$$

where $D_0 = 0,05$ mm is the wire diameter

$G$ is the mass velocity of fluid

$$G = \rho (T_{gas}) v(T_{gas}) = \rho_0 T_0 / T_{gas} \times v_0 T_{gas} / T_0 = 1,29 \times 0,3 \text{ kg/m}^2 \text{s}$$

$v_0 = 0,3$ m/s for a laminar flow methane-air flame

$\mu_f = 97,7 \times 10^{-6}$ Ns/m$^2$ is the viscosity for air at 1900 K

Fig 10-7, p.259 gives

$$h_m D_0 / k_f = 0,9 \Rightarrow h_m = 0,9 \times 0,0633 / 5 \times 10^{-3} = 1140 \text{ W/m}^2 \text{K} = \text{the surface coefficient for heat transfer}$$

where $k_f = 0,024$ W/mK is the thermal conductivity for air at 273 K, $k_f \sim T^{1/2} \Rightarrow k_f (T=1900 \text{ K}) = 0,024 \times (1900 / 273)^{1/2} = 0,0633 \text{ W/mK}$

$$A h_m \Delta T = A \varepsilon \sigma T^4 \Rightarrow \Delta T = 0,15 \times 5,67 \times 10^{-8} \times (1900)^4 / 1140 = 97 \text{ K}$$

where $A$ is the area

$\varepsilon \approx 0,15$ for PtRh at about 1900 K

$\sigma = 5,67 \times 10^{-8}$ W/m$^2$K$^4$ (Stefan-Boltzmann)

This shows that the PAMS measurement is very close to the thermocouple value, the difference being at the most about 50 K (cf. Fig 7).

PADS measurements

Apparatus

With reference now to Fig 8, the following apparatus was used.

The same laser system was used as in the PAMS measurements except that an additional He-Ne laser with an output of $\approx 5$ mW was used to probe the flame. The He-Ne beam was also focused by a $\approx 50$ cm.
Focus-length lens (L) and located essentially parallel to the UV beam (the angle approx. 1.5°). The distance from the lenses to the flame (B) was about 35 cm and the distance from the flame to the detector (D) was about 2.5 m. To shield the detector from the UV-light two filters (F) RG 610 and a tubular shield (S) were used.

The detector comprised four photosensitive quadrants. The current from two opposing quadrants in the direction of the deflection was fed into current-to-voltage amplifiers (cf. Fig 9) and then the signals were subtracted in a difference amplifier. The difference signal was filtered through a simple electronical filter with a 3 dB cut-off frequency at about 10 kHz. The signal from the detector was passed through an AC coupled pulse amplifier to match the 50 Ω oscilloscope input.

Measurements

The pump (YAG) beam and probe (He-Ne) beam were located a few millimeters above the burner. The probe beam was directed to the detector by a mirror and positioned at the center of the detector. At the center the ripple in the signal from the He-Ne laser reached its least value. The intensity of the YAG-laser was optimized by use of an ordinary power meter at a wavelength absorbed by the OH-radicals. The distance between the probe and pump beam was varied by rotating the Pellin-Brocca prisme until the deflection signal was observed on the oscilloscope screen (cf. Fig 10).

1. The signal was averaged through a boxcar integrator and recorded on a strip-chart recorder. The 5 μs gate was positioned at the negative peak of the signal. The signal was measured for different heights above the burner by moving the burner on a micrometer caliper.

The signal profile was similar to that obtained with the PAMS technique (cf. Fig 11).

2. By turning the wavelength dial on the dye laser in steps of 5 pm and subsequently optimizing the laser power a spectrum was obtained on the recorder. The averages were plotted in a diagram (cf. Fig 12) and some lines could be identified (cf. Fig 12 and 13).

However, due to the incertainty in the laser power (the strength of the UV-fluorescence was estimated on a piece of paper) may be somewhat inaccurate.

Discussion

Problems with the quadrant detector

A significant noise in the amplifier of the detector unit made it necessary to use a He-Ne laser with high power output (≈ 5 mW).

Unfortunately this particular laser had a ripple in the intensity level of ≈ 50% of the PADS signal, although the ripple was almost cancelled when
the beam was directed exactly in the middle of the detector (e.g. both
the operative quadrants were subjected to the same ripple signals,
which were subtracted from each other by the difference amplifier). The
ripple was probably due to to miss-match in the He-Ne power unit.
Also, it was necessary to shield the detector from the UV-light,
which was scattered in the room and caused a substantial signal (which
was initially mistaken for the PADS signal).
In order to photograph the signal a 50Ω input impedance oscilloscope
had to be used and an AC coupled pulse amplifier to match the input
impedance. With an ordinary 1MΩ oscilloscope the before mentioned
signal from the diffusion of heat was unclearly observed as an overall
displacement of the PADS signal.

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Studies - LRAP-22
Fig 1 shows the logarithm of the PA signal against the logarithm of the distance between microphone and burner.
a. Tuned to an absorption line, \( r = 4 \) cm.

b. Detuned, \( r = 4 \) cm.

c. The microphone is at \( r = 10 \) cm.

Fig. 2 shows photographs of the PA signal obtained with the slot burner, 50 \( \mu \)s and 0.2 V per division.
Fig 3 shows the set-up for the PAMS measurements.
Fig 4 shows photographs of the PA signal obtained with the flat flame burner with the laser tuned to an absorption line of OH.
Fig 5 shows the PA signal for different heights above the burner.
\[
\ln \frac{a}{A_{\text{nm}}} \]

Fig 6 shows an exemplary semi-logarithmic plot of the PA signal at the height \( h = 1.5 \) mm divided by the rotational transition probability against the rotational energy.
Fig 7 shows the temperature distribution in the flame, wherein the (+)-signs and the continuous line represents the PAMS measurement and the broken line represents the thermocouple measurement.
Fig 8 shows the set-up for the PADS measurements.
Fig 9 shows the electronical circuitry in the detector unit.
a. This is a shot with the pump beam slightly above the probe beam, 50mV - 0.5μs per div.

b. This is a shot with the pump beam crossing the probe beam (e.g., the noise signal), 20mV - 0.5μs per div.

c. This is a shot with pump beam below the probe beam, 50mV - 0.5μs per div.

d. This is a shot with the pump beam farther below the probe beam, 50mV - 0.5μs per div.

Fig. 10 shows photographs of the PADS signal at the strongest line at the wavelength 281.16 nm.
Fig 11 shows a comparison between PADS and PAMS signals.
Fig 12 shows an excitation spectrum of the OH-radicals obtained with PADS technique.