Fundamental Study of CARS Thermometry

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ABSTRACT

Spatial resolution of N₂ CARS thermometry was investigated in burner flames. The spatial resolution is approximately 100μm in diameter by 1mm long, and sharp temperature gradient of 4500K/mm was measured across the flame front.

Pressure dependence of N₂ CARS spectra was investigated using a high pressure, high temperature gas vessel. Using exponential gap law model, measured N₂ CARS spectra agreed closely with computer-synthesized spectra in the temperature range of 300-1000K and at pressures of 1-30atm.

CO CARS spectra were also computer-synthesized under high pressure conditions, the results providing similar to measured CO CARS spectra. Simultaneous measurement of CO concentration and temperature was found to be possible.

EXPERIMENTAL APPARATUS

CARS System

For the measurements to be described here, multiplex BOXCARS was arranged as shown in Fig.1. The output of a frequency doubled Nd:YAG laser was used to provide a pump frequency as well as to drive a Stokes shifted dye laser at a repetition rate of 10pps. At wavelength 532nm, the power of the pump beam was 100mJ/pulse, and the bandwidth 0.13cm⁻¹ (FWHM). The pump beam was split into two, the resultant beams being crossed through a 300mm focal length lens at a full angle of 1°. The Stokes beam was added at an angle that satisfies the phase matching condition.

CARS signals were separated from the laser beam by dichroic mirrors, dispersed by a 1.5m monochromator, and detected by an optical multi-channel analyzer (OMA2). A magnifier (x8) was added in front of the detector to improve the spectral resolution.

Burner

A premixed flame was obtained by a burner, special precautions being taken to ensure flame stability. The experimental setup of the burner is shown in Fig.2. A burner tube with inner diameter of 7mm was used in order to obtain a stable flame.

Fuel and air were conducted through capillary tubes to stabilize gas supply. Protective air was provided by a blower.

Fig.1 CARS experimental arrangement (BOXCARS)

Fig.2 Experimental setup of the burner

Gas Vessel

High pressure, high temperature gas was obtained by an electrically heated gas vessel, rated for temperatures up to 1000K and pressures up to 50atm. Fig.3 shows a schematic of the vessel. There is a quartz window on both side of the vessel. Temperature of the gas was controlled within 10K and monitored by thermocouple.
Fig. 3 Cross-section of the high pressure and high temperature vessel

The limited optical access provided by the vessel dictated a collinear alignment of the pump and Stokes beams used to generate CARS.

COMPUTER MODELING

Collisonal Narrowing

CARS spectra consist of many Q-branch lines. At low pressure, the spectral profile of CARS is determined by the position and width of isolated Q-branch lines, and the population difference between the upper and lower levels of vibrational Q-branch transitions.

For diatomic molecule, the position of Q-branch line is given by

$$v_J(J+1)$$

where $v_J$ is vibration rotation interaction constant (0.0187 cm$^{-1}$ for N$_2$)

There is little interaction between adjacent Q-branch lines at low pressure. However, interaction among isolated lines gradually increases as pressure rises because line widths broaden linearly with pressure. This is called pressure broadening and occurs at a rate of 0.1 cm$^{-1}$/atm for N$_2$. Collisonal narrowing is caused by the increased interaction as shown in Fig. 4.

Modelling

In the field of Raman spectroscopy, theoretical studies of collisional narrowing were carried out by Alekseyev et al. and Brueck et al. Recently Hall et al. applied these theories to CARS.

Our computer modeling was based on Hall’s study, except for changes in parameters associated with experimental details and molecular constants CARS intensity $P(\omega)$ at frequency $\omega$ is given by the following equation:

$$P(\omega) \propto \int f_1(\omega) d\omega \int f_2(\omega) |C(\omega)|^2 d\omega$$

where $f_1$ and $f_2$ are spectral profiles of the pump and Stokes beam.

$C(\omega)$ is third-order nonlinear electric susceptibility.

Fig. 4 Energy level diagram of CARS spectrum

The spectral profile of CARS is governed by $X^{(3)}$. Therefore, the production of CARS spectra requires a mathematical expression of $X^{(3)}$.

Four types of models were computed as follows:

Excluding collisional narrowing, isolated line

Including collisional narrowing

1. Diffusion model

$$X^{(3)} = -\frac{\lambda}{\rho^{(0)}(\omega)} \sum_{i=1}^{n} \delta (\omega - \omega_i)$$

2. Inverse power law model

$$X^{(3)} = -\frac{\lambda}{\rho^{(0)}(\omega)} \sum_{i=1}^{n} \left(\frac{\omega - \omega_i}{\rho^{(0)}(\omega)}\right)^{-\gamma}$$

3. Exponential gap law model

$$X^{(3)} = -\frac{\lambda}{\rho^{(0)}(\omega)} \sum_{i=1}^{n} \left\{\frac{\omega}{\rho^{(0)}(\omega)}\right\}^{-\gamma}$$

The $T$, $P$, and $J$-dependence of collisional Raman line width are very important in interpreting CARS spectra in high pressure conditions. In our calculations, high pressure Raman line widths were extrapolated from low pressure data measured by Khan and Owyoung.

The approximation of the Raman line width is as follows:

$$\Gamma = a(T) + b(T) \Gamma + \Gamma_0$$

where $a(T)$ and $b(T)$: Parameters shown in Table 1

<table>
<thead>
<tr>
<th>$\Gamma$</th>
<th>Doppler width</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_0$</td>
<td>$\Gamma_0$</td>
</tr>
</tbody>
</table>

For reference, Hall's approximation is as follows:

$$\Gamma = 8T^{0.7} \times 18.6 \times 10^{-3}$$
Approximate Raman line width based on the data determined by Rassaco, Belbruno and Jammu used for our prediction of CO CARS spectra is as follows:

\[ \Gamma = \left( -2.42 \times 10^{-3} T + 0.083 \right) \pi \]

<table>
<thead>
<tr>
<th>T</th>
<th>a(T)</th>
<th>b(T)</th>
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</thead>
<tbody>
<tr>
<td>300</td>
<td>0.112</td>
<td>2.79x10^3</td>
</tr>
<tr>
<td>700</td>
<td>0.077</td>
<td>1.79</td>
</tr>
<tr>
<td>1100</td>
<td>0.055</td>
<td>7.24x10^2</td>
</tr>
<tr>
<td>1500</td>
<td>0.044</td>
<td>4.62</td>
</tr>
<tr>
<td>1900</td>
<td>0.038</td>
<td>3.28</td>
</tr>
<tr>
<td>2300</td>
<td>0.033</td>
<td>2.48</td>
</tr>
</tbody>
</table>

**TABLE 1**

Parameter of Raman line width

Fig. 5 shows the radial temperature profile of the flame. Measurements were taken 5.4 mm above the burner, starting from the center-line of the flame.

The observed profile shows a rapid rise in temperature in the flame front and a gradual decline in the outer diffusion zone. The insert is a blow up of the temperature profile across the flame front, which was measured about 650 μm.

**Pressure Dependence of N₂ CARS Spectra**

Fig. 6 shows effect of collisional narrowing at 300K. The dotted lines represent computer-synthesized spectra of isolated lines, which are not considered collisional narrowing. Fig. 7 shows a comparison between actual measurement of bandwidth and synthesized bandwidth based on isolated lines.

The measured bandwidths are smallest at 2 atm and gradually increase as pressure rise to 10 atm, remaining virtually constant thereafter. The effect of collisional narrowing may be slightly observed even at 1 atm. Figs. 8 and 9 show a comparison between the measured and predicted spectra at 1 and 30 atm respectively. A similar comparison is made for bandwidths (FWHM) in Fig. 10.

**RESULTS AND DISCUSSIONS**

**Burner Study**

To obtain temperature profiles in the premixed flame, the position of the flame relative to the laser beam intersection was changed horizontally and vertically. The displacement was in 50 μm steps the vicinity of the flame front. The CARS spectra were accumulated in the OMA for 20 to 180 pulses depending on the signal strength.

2-4 measurements were taken at each displacement step. The measured flame temperatures are accurate to be within ±50 K.

![Fig. 5 Radial temperature profile in a premixed flame](image)

![Fig. 6 Effect of collisional narrowing (at 300K)](image)

![Fig. 7 Comparison of predicted bandwidth by isolated line approximation and experiment](image)

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Fig. 8 Comparison of the theoretical models at 1 atm

Fig. 9 Comparison of the theoretical models at 30 atm

Fig. 10 Comparison of experimental and theoretical bandwidth (FWHM)

As may be seen from these comparisons, the spectra predicted by the exponential gap law model agree with the measured spectra throughout the whole pressure range. On the other hand, the spectra predicted by the other two models tend to be broader than the measured spectra. In particular, the rotational diffusion model, which is commonly applied to high density media (e.g., liquide), has a large error at high pressures.

These results are somewhat different from Hall's study, which shows good theoretical fit by the inverse power law model.

Fig. 11 shows measured N2 CARS spectra bandwidth compared to spectra bandwidth synthesized by exponential gap law model at temperatures of 300K, 600K and 1000K, and at pressure of 1 to 50 atm.

Fig. 11 Comparison between experimental and theoretical N2 CARS bandwidth at 1/2 and 1/3 of the maximum height

The bandwidth are measured at 1/2 and 1/3 of the maximum height. At half maximum height, predicted bandwidths are wider than measured bandwidths at high temperatures and high pressures. At 300K, the predicted bandwidths agree with the measured bandwidths as previously stated. At 1/3 of maximum height, the predicted bandwidth agree with the measured bandwidths throughout the whole range. In our calculation, Raman line width was extrapolated from Rahn and Owyoung's data measured under low pressure conditions. The difference in agreement between 1/2 and 1/3 maximum height is thought to be caused by J-dependence of Raman line width in high pressure conditions. Further studies will have to be made to resolve this problem.

No measurements could be taken at temperatures in excess of 1000K owing to the limitation of the vessel. Synthesized results show that a hot band peak appears when temperature exceed 1000K.

Fig. 12 Effect of collisional narrowing (at 2400K)

Fig. 12 gives the predicted N2 CARS spectra at a temperature of 2400K and pressures of 1 and 30 atm. Fig. 13 shows relative hot-band intensity at temperatures of 1500K, 2000K, and 2400K and pressures of 1 to 50 atm. The hot-band intensity increases substantially as the temperature rise. It is therefore possible to accurately determine temperature from the hot-band intensity.

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The effects of diluent gases on \textit{N}_2\text{ CARS spectra} were also studied. Fig.14 shows the \textit{N}_2\text{ CARS spectra of a mixture of 5\% \textit{N}_2 and 95\% diluent gases (He, Ar, CH\textsubscript{4}) at a temperature of 300K and a pressure of 10\text{atm}. He and Ar have little affect on \textit{N}_2\text{ CARS spectra, but CH\textsubscript{4} changes \textit{N}_2\text{ CARS spectra substantially, because of the large nonresonant susceptibilities of the same order as methane.}

The nonresonant susceptibility coefficients of certain gases are given in Table 2.

**Fig.14 Effect on diluent gases on \textit{N}_2\text{ CARS spectra}**

When measuring actual engine combustion temperatures, the effect of hydrocarbon nonresonant susceptibility must not be neglected, and nonresonant background must be suppressed by the method known as polarization CARS.

**TABLE 2**

<table>
<thead>
<tr>
<th>Component</th>
<th>Dielectric susceptibility coefficient</th>
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<tbody>
<tr>
<td>He</td>
<td>0.087 (cm(^3)/erg\times10^{18})</td>
</tr>
<tr>
<td>Ar</td>
<td>1.55</td>
</tr>
<tr>
<td>\textit{N}_2</td>
<td>1.75</td>
</tr>
<tr>
<td>\textit{O}_2</td>
<td>1.30</td>
</tr>
<tr>
<td>CH\textsubscript{4}</td>
<td>1.80</td>
</tr>
<tr>
<td>CO</td>
<td>2.95</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>2.00</td>
</tr>
<tr>
<td>NO</td>
<td>4.20</td>
</tr>
</tbody>
</table>

**Fig.15 Comparison between experimental and theoretical CO CARS bandwidth at 1/2 and 1/3 of the maximum height**

**Pressure Dependence of CO CARS Spectra**

Fig.15 shows CO CARS spectra bandwidths of measured and computer-synthesized spectra at temperatures of 300K, 600K, and 1000K, and pressures of 1 to 10\text{atm}. There is close agreement between the predicted bandwidths and the measured bandwidths. The temperature and CO concentration in the combustion chamber can therefore be determined from a prediction having the same profile. Background suppression technique must be used for the combustion chamber measurement, because as shown in Fig.16 the effect of nonresonant background due to the diluent gases is very strong.

**Fig.16 Temperature dependence of diluted CO CARS spectra at 30\text{atm}**

**SUMMARY**

This paper demonstrates that the temperature profile across a narrow flame front in premixed flame at atmospheric pressure can be explored with a conventional \textit{N}_2\text{ BOXCARS.}

Spatial resolution is estimated to be 100\text{um}, while the flame front is about 650\text{um} thick in a stoichiometric methane flame.

Studies of thermometry in high pressure conditions were conducted and it was shown that the effects of pressure are accurately predicted at bandwidths of 1/3 maximum height by exponential gap law model based on collisional narrowing.

The effect of diluent gases was also studied, and it was found that nonresonant background must be suppressed. CO CARS spectra were predicted and compared with measured spectra throughout a wider pressure range. The close agreement indicates that CO concentration and temperature may be determined from a prediction with the same profile.
REFERENCES