

Multiplex polarization spectroscopy of OH for flame thermometry

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Abstract. Multiplex polarization spectroscopy is demonstrated and applied to thermometry of a methane/air flame. Using a broad bandwidth, modeless laser, single-shot spectra of OH were recorded showing several transitions from the $A^2\Sigma - X^2\Pi(0,0)$ band system. High resolution polarization spectra were also recorded in the same flame using a conventional, frequency scanned, narrow linewidth dye laser. Absorption effects were found to produce significant systematic errors in the temperatures derived from the unsaturated spectra produced by both multiplex and narrow linewidth scanning techniques. After correction for absorption effects, temperatures were derived from the single-shot multiplex spectra with a precision of 4% which agreed well with values obtained from scanned spectra and from the calculated adiabatic temperatures.

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Optical and spectroscopic techniques, particularly laser based methods, are now used widely for diagnostics of hostile environments. They can provide remote, non-intrusive, spatially and temporally resolved measurements of parameters important for understanding the complex chemical and dynamical processes occurring in combustion or plasmas. Linear effects such as spontaneous Raman scattering and laser induced fluorescence, LIF, and non-linear processes such as coherent anti-Stokes Raman scattering, CARS, have been applied successfully and have been reviewed in the context of combustion diagnostics [1]. Resonant spontaneous processes such as LIF are applicable to detection of minor species whereas coherent, non-linear, processes such as CARS are usually restricted to use with majority species. Degenerate four wave mixing, DFWM, was introduced as a coherent, non-linear, technique for the detection of minor species [2]. DFWM is experimentally simpler to implement than fully resonant CARS [3] which also uses strong dipole resonances to enhance sensitivity.

More recently polarization spectroscopy, PS, has been used for detection and thermometry of minority species in flames [4, 5]. Both DFWM and PS share the coherence advantages of CARS but, as fully resonant processes, their sensi-

tivity is comparable to that of LIF and consequently may be used to detect trace species and short lived radicals present in flames and plasmas. PS has an additional simplicity compared to DFWM as only two beams, rather than three, are required to interact in order to generate a signal. However, the PS signal is strongly affected by birefringence in optical components, such as containment windows, and the technique is presently suitable only for open flames. High resolution spectra are recorded using either DFWM or PS by scanning the frequency of the incident narrow bandwidth laser light used to generate the signal. In situations such as turbulent flames, where conditions change rapidly in time, it is desirable to make instantaneous temperature measurements. Multiplex CARS is a well established technique for single-shot temperature measurements using majority species [6]. Two-line techniques, using a dual-wavelength laser, have been demonstrated for single-shot thermometry in flames using both DFWM and PS [7]. Broadband or multiplex DFWM [8] has been demonstrated and applied to single-shot thermometry using minor species OH [9, 10] and C_2 [11] radicals in flames.

In this paper we report the first demonstration of multiplex polarization spectroscopy and its application to single-shot flame thermometry. Polarization spectra involving several transitions in the $A^2\Sigma - X^2\Pi(0,0)$ band of OH were obtained in a methane/air flame and flame temperatures were derived from a Boltzmann plotting method. Temperatures were measured in the same flame using narrow bandwidth PS for comparison with the results of the multiplex technique. Problems arising from absorption effects on the incident and signal beams are discussed for both narrowband and broadband excitation and difficulties encountered with simultaneous referencing of the laser spectrum in multiplex PS are described.

1 Theory

Polarization spectroscopy was introduced as a means of obtaining low background, Doppler-free spectra [12]. The signal is provided by a weak, linearly polarized, probe beam passed through a normally isotropic medium which is simultaneously irradiated with a strong, counter-propagating, pump beam

having the same frequency as the probe. A linear polarization analyzer is set to be orthogonal to the initial polarization state of the probe, resulting in zero transmission to the detector. When the pump and probe laser beams are tuned to resonance with an electronic transition in the medium, an anisotropy is induced by the pump beam which depends on the polarization state of the pump. The anisotropy is a result of selective depopulation of different magnetic sublevels in the initial electronic level involved in the transition. The resulting birefringence or dichroism of the medium leads to a rotation of the plane of polarization of the probe beam or a degree of ellipticity in its polarization state. In either case some component of the probe beam is transmitted to the detector and registers the resonant interaction. For incident laser intensities less than the saturation intensity, I_{sat} , and in the absence of absorption effects, when the analyzer is perfectly crossed with the initial polarization direction of the linearly polarized probe, and there is negligible background birefringence arising from other optical components, the signal intensity transmitted by the analyzer is given by [12, 13].

$$I_{\text{sig}} \propto I_{\text{las}}^3 N_0^2 B^4 \xi^2 \quad (1)$$

where I_{las} is the laser intensity, N_0 is the population of the lower state, B is the Einstein B coefficient and ξ is a J dependent numerical factor which is tabulated in [14]. The numerical factors take large values for R and P lines for a circularly polarized pump beam and large values for Q lines for a linearly polarized pump beam. In this work a circularly polarized pump beam was used to excite transitions in the R_1 bandhead of OH. A more sophisticated theory of PS using monochromatic excitation has recently been developed and shown to predict spectra in good agreement with those recorded in OH and NH [15]. Equation (1) shows that the signal intensity, I_{sig} varies as the cube of the laser intensity for $I < I_{\text{sat}}$ and as the square of the lower level population. The temperature may be derived, assuming a Maxwell-Boltzmann distribution for the level populations, from a plot of $\ln [I_{\text{sig}} / (2J + 1)^2 B^4 \xi^2 I_{\text{las}}^3]$ versus Ehc/k , where E is the energy of the lower level of the transition. This Boltzmann plot yields a straight line with gradient $-2/T$. The advantage of this technique is that a departure from Maxwell-Boltzmann statistics is indicated by a deviation from a straight line on the Boltzmann plot.

At present no theory of broadband PS is available. In the case of broadband DFWM the results of broadband theory agree in related respects with the results of monochromatic theory for non-saturating incident fields [16]. In the present work involving broadband PS the dependence of the relative spectral intensity of each transition in multiplex spectra is assumed to be the same as that predicted for monochromatic excitation. Care was taken in obtaining experimental data to ensure that no significant saturation was occurring.

2 Experiment

The experimental arrangement for multiplex PS is shown schematically in Fig. 1. The broadband radiation was provided by a modeless laser [17] pumped by a frequency-doubled Nd:YAG laser (Spectra-Physics GCR-4) operating at 10 Hz. The modeless laser (Mode-x Laser Systems), ML, emits an essentially continuous spectrum which is ideally

suited to multiplex spectroscopies such as CARS [18, 19] and DFWM [11]. In the present work the ML used a methanol solution of sulforhodamine and the output was tuned, and bandwidth limited, by an internal interference filter. The output was frequency-doubled to yield a pulse of bandwidth around 0.1 nm and an energy of 0.5 to 1.0 mJ. Pulse energies in the interaction region were limited to typically 15 μJ for the probe and 150 μJ for the pump beam. The centre wavelength of the broadband output was tuned to excite transitions in the $A^2\Sigma - X^2\Pi(0,0)$ R_1 bandhead of OH. Pump and probe beams were arranged to cross in the "forward geometry", i.e. both beams travelled in the same general direction through the flame, crossing at a small angle.

The broadband UV beam was split using two surface reflections to provide two weak beams; one to serve as the probe beam, the other as the reference beam, with the remainder of the energy being used as the pump beam. The probe beam was focused by a 500 mm focal length lens into the interaction region and its polarization was defined by passing through a Glan-Thomson prism. The reference beam was focused into a 500 μm aperture optical fibre which conducted the light to a different position on the spectrograph entrance slit from that on which the signal was incident. Thus the spectra of both signal and reference spectra could be recorded simultaneously by the CCD camera. The pump beam was passed through a half-waveplate/polarizer assembly to provide continuous adjustment of its intensity, through a quarter wave plate to produce circularly polarized light and focused into the interaction region by a 500 mm focal length lens.

The probe beam, having emerged from the interaction region defined by its overlap with the strong circularly polarized pump, passed through a high extinction ratio (better than 10^6) linear analyzer (Halle) before being recollimated and focused onto the entrance slit of a 1 m Czerny-Turner spectrograph (Hilger). The critical phase matching used for frequency-doubling the ML output introduces some dispersion across the beam owing to the finite beam divergence of the dye laser output. The direction of this dispersion was arranged to be parallel to the spectrograph slit in order to minimize any vignetting of different spectral components in the signal by the 75 μm entrance slit.

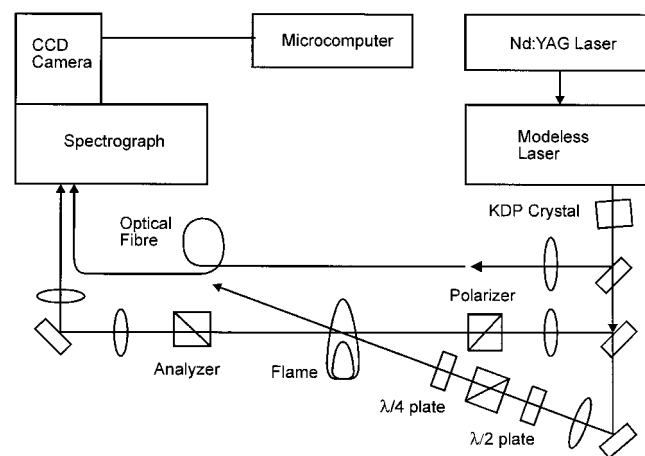


Fig. 1. Experimental setup used for multiplex polarization spectroscopy of OH for flame thermometry

The spectrograph, equipped with a 2400 lmm^{-1} holographic grating, was operated in second order and spectra were recorded using an unintensified CCD camera (Princeton Instruments) fitted with a mechanical shutter. The minimum exposure time for this shutter was 0.2 s but the flame luminosity was sufficiently low that negligible background light was recorded during the shutter opening time. The CCD chip was thermoelectrically cooled to 0°C to reduce pixel noise which was typically 10 counts.

The pump and probe beams crossed at an angle of 6° and the focused beam diameter of approximately $500\ \mu\text{m}$ gave an interaction length of approximately 5 mm.

The interaction region was arranged to lie in the premixed methane/air flame formed on a Bunsen type burner having a nozzle diameter of 10 mm. Two different gas mixtures having stoichiometry of $\phi = 1.2$ and 1.6 were used to produce flames with adiabatic temperatures of 2205 K and 1853 K respectively. Two regions of the flame, of differing thickness, were investigated in order to study the effects of absorption on the PS signals.

Precise alignment of the signal and reference spectra with the spectrograph was found to be a critical factor in obtaining reproducible results. Owing to the relatively narrow laser spectrum used in this work and the open nature of the OH spectrum, the signals tended to be generated on the edges of the laser spectrum where the gradient of the laser spectrum was largest. Thus small deviations of registration between signal and reference spectra had a marked effect on derived temperatures.

The high quality analyzer was adjusted to be optimally crossed with the polarizer in the probe beam by minimizing the transmitted intensity detected by the CCD camera on the output of the spectrograph. By careful adjustment the background intensity level, resulting from leakage through the analyzer, could be reduced to less than the pixel noise on the CCD chip. Using the shortest exposure time available with the mechanical shutter of 0.2 s, the spectra recorded were the sum of two successive laser shots. By using an additional chopper wheel, single-shot spectra could be isolated.

The saturation behaviour of the spectra was observed by measurements on the $R_1(5)$ line using a constant probe intensity and variable pump intensity. In this way the regime where the signal was proportional to the square of the pump intensity was identified, and all subsequent spectra were recorded in this non-saturating regime.

Narrow bandwidth polarization spectra were obtained by replacing the broadband modeless laser with a conventional, narrow linewidth dye laser (Spectra-Physics, PDL-3). The frequency-doubling crystal was automatically scanned, to optimize the second harmonic generation as the dye laser frequency was tuned, by use of an auto-tracking device (Inrad). Pump and probe beams were unfocused and crossed in the same co-propagating geometry as used for the multiplex PS experiments. The incident laser intensity was maintained below the measured saturation levels. The PS signal was detected by a photomultiplier and recorded using a boxcar averager system (Stanford Research Systems, SR250).

Narrowband and broadband PS spectra were recorded in two regions of the Bunsen flame viz. just above the primary reaction zone and also at the base of the flame. In the first region the flame opacity at the linecentres of the main resonances in the OH spectrum was measured to be approxi-

mately 30%, whereas at the base of the flame the absorption was found to be between 5% and 10%. With a fuel-rich mixture (ϕ approximately equal to 1.2) the OH concentrations in a methane-air flame peak in the range 10^{-3} – 10^{-2} mole fraction [20]. These concentrations are consistent with the absorption measurements in the present work.

3 Results and discussion

A typical single-shot multiplex PS spectrum generated at the base of the flame in the region of the $A^2\Sigma - X^2\Pi(0,0)$ R_1 bandhead of OH is shown in Fig. 2. Spectra recorded at both the top and bottom of the flame showed significant effects of absorption. The influence of absorption on resonant DFWM has been noted previously [21] and procedures have been developed to allow temperatures to be corrected for such effects [22].

According to the Beer-Lambert Law, on passing through an absorbing medium of length L , a beam of intensity I_0 will emerge with intensity I such that:

$$I = I_0 \exp \left[\int_0^L -\epsilon c(l) dl \right] \quad (2)$$

where ϵ is the absorption coefficient and $c(l)$ is concentration of the absorbing species. The pump and probe beam intensities at the interaction region and the emerging signal beam intensity will be reduced by absorption. The magnitude of these effects is critically dependent on the position of the interaction region within the flame [22]. We assume that the absorption length is equal for all three beams (equal to one flame radius) which is a reasonable approximation for measurements made at the top of the flame. Measurements made at the base of the flame involve the beams crossing either at the front or the back of the cone of unburnt gas. Spectra generated at both front and back of the cone, and temperatures derived therefrom, did not differ significantly and so we assume the

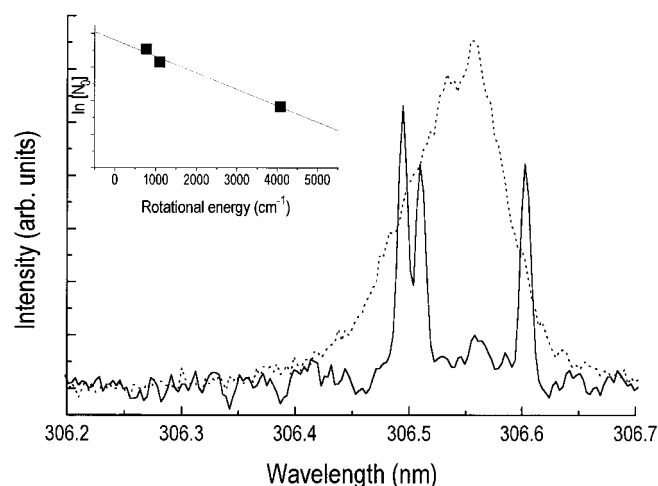


Fig. 2. Single shot multiplex PS spectrum of lines $R_1(6)$, $R_1(12)$ and $R_1(5)$ in the OH spectrum. The laser intensity is superimposed on the spectrum. The Boltzmann plot for this spectrum is shown inset after correction of each point for absorption. A least squares regression fit to these points is shown which gave a single shot temperature of 2050 ± 270 K

symmetrical case for simplicity. The incident laser intensity in (1) will be modified according to (2) and the corrected signal intensity will be given by:

$$I_{\text{sig}} \rightarrow \frac{I_{\text{sig}}}{\exp \left[\int_0^R -\epsilon c(l) dl \right]} \quad (3)$$

where R is the flame radius.

Applying the correction for absorption to the data shown in Fig. 2 allows a corrected Boltzmann plot to be drawn and this is shown inset to the figure. The temperature derived from this plot is 2050 K with an error of ± 270 K. Sets of 100 single-shot or double-shot spectra were analyzed to determine the precision of the technique. A histogram of temperature values derived from a typical set is shown in Fig. 3. The mean temperature is 2190 K with a standard deviation of 90 K (corresponding to $\pm 4\%$) in reasonable agreement with the calculated adiabatic temperature of 2205 K. With a different stoichiometric mixture the measured temperature had a mean value of 2120 K compared to a calculated adiabatic value of 1850 K.

For comparison, in Fig. 4 we show data obtained from a narrowline PS spectrum recorded in the base of the flame. The Boltzmann plots are shown with and without the correction for absorption which reduces the inferred temperature from $2530 \text{ K} \pm 200 \text{ K}$ to $2270 \text{ K} \pm 80 \text{ K}$ for a flame with a theoretical temperature of 2205 K. For the lower temperature flame having a theoretical temperature of 1850 K the mean

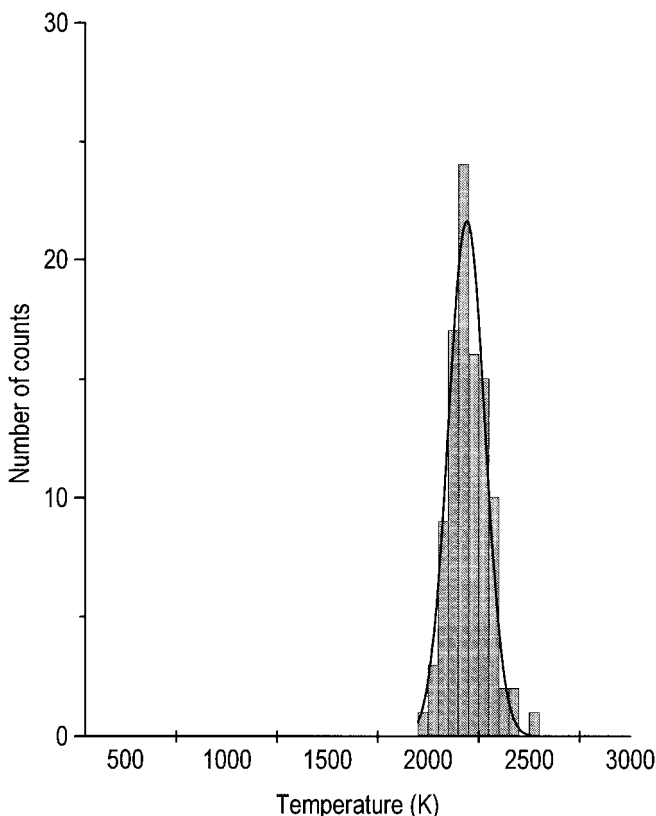


Fig. 3. Typical histogram of temperatures obtained from 100 double laser shot multiplex PS spectra. The solid line indicates the Gaussian distribution of this data giving a mean temperature of 2190 K with a standard deviation of 90 K

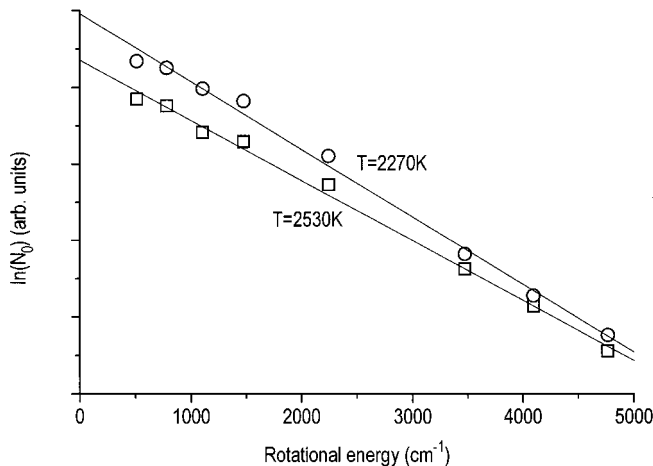


Fig. 4. Boltzmann plot for the narrow bandwidth PS spectrum of the R_1 bandhead of OH. The circular symbols are for data that have been corrected for absorption through the flame. The solid lines are linear regression fits to the corrected and uncorrected data. The two fits yield temperatures of 2270 K and 2530 K for the corrected and uncorrected data respectively

value, corrected for absorption, was 1955 K with an error of $\pm 150 \text{ K}$.

In the region of the flame above the primary reaction zone, the absorption is much stronger and its effects on the measured temperatures both more pronounced and more difficult to correct. In the higher temperature flame (2205 K) the uncorrected value obtained from narrowline PS was $3330 \text{ K} \pm 320 \text{ K}$ which is corrected to $2180 \pm 130 \text{ K}$. The results obtained using broadband PS in this region of the same flame were $3056 \pm 200 \text{ K}$, corrected to $2220 \pm 100 \text{ K}$.

These results show the dramatic effects of absorption on unsaturated PS for both narrow and broad bandwidth excitation. A simple correction to allow for the absorption yields temperature values in reasonable agreement with calculated values based on the mixture stoichiometry.

A major source of error in the present technique stems from the difficulty of producing a sufficiently broad spectral bandwidth to excite the widely spaced OH lines with equal intensity. For some data sets the laser bandwidth was sufficient to generate signals on only two of the widely spaced R_1 lines in the spectral region studied here. It was found that the $R_1(6,12)$ pair gave more accurate results than the $R_1(5,13)$ pair, i.e. more in agreement with the temperature derived from the narrow line scans over a wide range of the R_1 band. The reason for this discrepancy is not understood at present. The most accurate and reliable results were derived from spectra consisting of at least three lines e.g. $R_1(5,6,12)$.

Secondly, the effects of absorption lead to large systematic errors in the measured temperature. We note that all the temperatures measured using the PS technique, both narrowband and broadband, were consistently higher than expected. The simple correction procedure adopted did bring the values into more acceptable agreement with those expected. However since the corrected values remain systematically high this simple procedure appears not to account completely for the absorption effect. Improvements in accuracy would require a quantitative theoretical description of these absorption effects on the PS signal and a detailed knowledge of the distribution of the species responsible for the absorption.

Finally, the concentration of OH in a flame is known to fall dramatically with decreasing temperature. Since PS signals are quadratically dependent on the concentration, the steep temperature gradients encountered in Bunsen type flames result in the observed signal being generated almost entirely from regions of the flame above 1500K. Contributions to the signal from colder areas of the flame within the interaction region are insignificant and have been neglected in the present analysis.

In conclusion we have demonstrated that broadband or multiplex PS is a viable technique for single-shot thermometry of flames. Multiplex PS of OH in a methane/air flame has yielded temperatures in reasonable agreement with values obtained from narrow bandwidth PS when corrected for absorption and also with calculated values. The technique may be useful in optically thin flames and where a species can be probed with a convenient wide bandwidth laser source.

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