

# Thermometry of an oxy-acetylene flame using multiplex degenerate four-wave mixing of $C_2$

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**Abstract.** Thermometry of an oxy-acetylene flame using multiplex Degenerate Four-Wave Mixing (DFWM) of  $C_2$  is demonstrated. More than 100 rotational transitions in the  $d^3\Pi_g \leftarrow a^3\Pi_u(0,0)$  Swan band of  $C_2$  could be recorded simultaneously by use of a pulsed, broad bandwidth “modeless” laser. Temperatures were inferred by fitting temperature-dependent synthetic spectra of single- or multiple-shot averaged spectra. The strength and reliability of recorded signals together with the large number of rotational lines observed suggest that multiplex DFWM is a promising technique for minor species detection and for temporally resolved temperature measurements in luminous environments. Factors influencing the accuracy and precision of single-shot thermometry using the technique are discussed.

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The measurement of temperature and species concentrations is of major importance in the study of combustion and plasma processes. Temperature is a key parameter for model validation, simulation and improvement of practical combustion and industrial plasma devices. Laser-based techniques for thermometry are valuable tools since they offer high spatial and temporal resolution and, most importantly, are non-intrusive. Spontaneous Raman scattering, Coherent Anti-Stokes Raman Scattering (CARS) and Laser Induced Fluorescence (LIF) have all been successfully applied to the determination of temperature distributions in flames, internal combustion engines and other hostile environments. Applications, relative advantages and disadvantages of these techniques have been extensively reviewed [1].

More recently, Degenerate Four-Wave Mixing (DFWM) [2, 3] and polarization spectroscopy [4, 5] have been applied to minor species detection and temperature measurements in flames. These techniques share the coherence advantages of CARS but as single-photon

resonant processes they have a sensitivity which is comparable to that of LIF and so may be used to detect chemical intermediates occurring at trace levels in plasmas and flames. The application of these techniques for the detection of  $C_2$  in atmospheric pressure oxy-acetylene flames has been reported recently [6, 7].

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 and accurate technique for this purpose but its application is restricted to majority species [8]. The possibility of multiplex DFWM has also been demonstrated [9] and applied to thermometry using the OH radical [10, 11]. In previous work in our laboratory, a broad bandwidth “modeless” laser [12] was used to excite simultaneously several transitions in the OH radical in a laminar methane/air flame. However, the relatively open structure of the OH spectrum restricted the number of transitions that could be simultaneously probed, owing to the limited bandwidth in the frequency-doubled broadband laser, and so limited the accuracy of the method. Additional uncertainties were introduced by the poor beam quality and effects of spatial variation of the spectral content arising from critical phase matching used for the frequency doubling [13].

In the present work, the application of multiplex DFWM to probe the  $C_2$  radical is demonstrated. Transitions in the  $C_2$  Swan bands lie in the visible spectral region and so may be conveniently excited using high-gain dye lasers. Problems associated with the frequency doubling, which was necessary to excite transitions in OH, may thus be avoided.  $C_2$  was detected in an atmospheric pressure oxy-acetylene flame by multiplex DFWM using a “modeless” laser having a variable bandwidth sufficient to encompass many transitions in the Swan bands in a single shot.

## 1 Theory

A general theoretical treatment of multiplex DFWM requires that the effects of field fluctuations, inherent in the

broad bandwidth of the laser used, be taken into account. A solution of this problem has been presented for the case of a laser field whose bandwidth exceeds all other relaxation rates in the interaction with a two-level atom [14]. The signal intensity and saturation behaviour [14], temporal response [15] and spectral profile of the signal [16] have been derived using appropriate approximations and solved numerically. For thermometry the interpretation of multiplex spectra requires knowledge of the signal dependence on laser intensity and the transition dipole moment  $\mu$ . In the case of low intensities, an analytic solution of the broad bandwidth problem is possible [14] and is found to have the same intensity and dipole moment dependence as for the more familiar case of monochromatic excitation [17]. The standard theory of DFWM in absorbing media, appropriate to monochromatic laser fields, considers a homogeneously broadened system consisting of two levels to which a nearly resonant monochromatic laser field is coupled [18]. The observed DFWM signal intensity is governed by the ensemble average of the electric dipole moments induced in the medium. In the limit of low absorption and weak probe fields this problem can be solved analytically for arbitrary pump intensities by use of a perturbative treatment.

For pump intensities much less than the saturation intensity,  $I_{\text{sat}}$ , the signal intensity scales as the cube of the laser intensity,  $I$ . For increasing pump intensities the DFWM signal starts to deviate from this cubic power dependence until at  $I \gg I_{\text{sat}}$  (complete saturation) the signal becomes independent of laser power. Between these two regimes it is found that the signal dependence on the dipole transition moment  $\mu$  changes drastically [17]. At low intensities,  $I \ll I_{\text{sat}}$ , it follows a  $\mu^8$  dependence whereas for  $I \gg I_{\text{sat}}$  it scales as  $\mu^2$ . Thus the quantitative interpretation of the relative signal strength from different transitions is complicated by the fact that the line strength ( $\propto \mu^2$ ) may vary for the different transitions. In practice, the exact nature of the dipole dependence is often not required since the change over the range of interest may be negligible. In all intensity regimes the DFWM signal is proportional to  $N^2$ , where  $N$  is the number density of the ground-state population (assuming negligible thermal population of the upper level). For temperature measurements the relative signal intensities of different rotational lines are compared. These intensities are proportional to the square of the population distribution over the rotational levels in the lower state. In thermal equilibrium, this distribution is governed by a Boltzmann distribution and hence the temperature may be inferred.

For the synthesis of theoretical spectra it was assumed that intensities of overlapping lines could be added. Lorentzian lineshapes were centred on individual line positions taken from the literature [19]. This lineshape function was determined by fitting to recorded isolated lines. The recorded linewidth is determined principally by the resolution of the monochromator and the pixel size of the CCD chip ( $\sim 0.7 \text{ cm}^{-1}$ ).

Recently, it was shown that the induced dipole transition moment depends on the relative orientation of the polarization of probe and pump beams [20]. A very weak level dependence of these geometrical effects was also established which differs for different geometries.

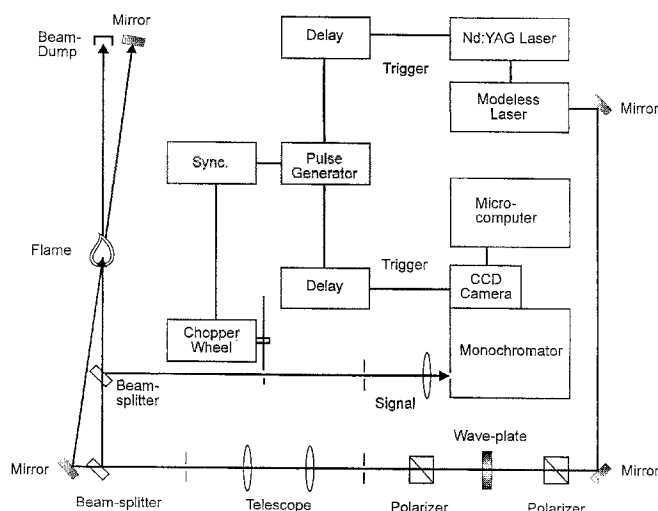


Fig. 1. Experimental setup used for thermometry in  $\text{C}_2$  using multiplex DFWM spectroscopy

These effects are negligible for the large  $J$  values used in the present work [21].

A minimization routine (NAG E04JAF) was used to perform a least-squares fit of the simulated, temperature dependent spectra to the experimentally recorded spectra.

## 2 Experiment

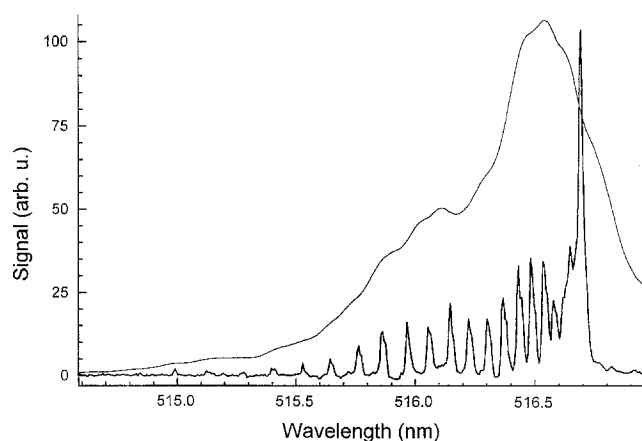
The standard retroreflecting geometry for DFWM was used in these experiments and the experimental arrangement is shown schematically in Fig. 1. Two counter-propagating pumps are crossed in a horizontal plane at an angle of ( $\sim 15^\circ$ ) by a weak probe beam. The signal retraces the path of the probe and is picked off by a 50% beam-splitter. No polarization discrimination was used and all beams were horizontally polarized.

Broad bandwidth radiation was provided by a "modeless" laser, ML [12]. This device has no optical resonator and therefore no longitudinal mode structure is imposed on the output of the device. Mode competition effects in conventional lasers lead to phase and amplitude fluctuations which contribute spectral noise and complicate the interpretation of multiplex molecular spectra. In multiplex CARS thermometry, the reduction of this spectral noise, by use of a ML, has been shown to increase the precision of single-shot temperature measurements [22, 23]. In the present experiment, the ML was operated close to 516 nm to excite transitions in the  $d^3\Pi_g \leftarrow a^3\Pi_u(0,0)$  Swan-band system of  $\text{C}_2$ . The ML was operated with Coumarin 500 dye (Exciton) dissolved in methanol and wavelength selection and spectral narrowing was achieved using a diffraction grating in the device. The laser was pumped with the frequency-tripled output of a Nd:YAG laser (Spectron Laser Systems) providing 45 mJ at 355 nm (10 Hz,  $\sim 7$  ns pulse duration). This pump energy was divided so that 15 mJ was used to pump the ML seeder and the rest to transversely pump a single amplifier stage. An output energy of 6 mJ of tunable radiation was obtained from the ML system with the centre frequency

tunable over a range of 15 nm. The bandwidth was determined by the grating angle and the type of diffraction grating used and could be adjusted continuously from 1 to 5 nm. In all experiments described either 600 or 300 lines/mm blazed gratings were used.

A polarizer-waveplate assembly was used to provide continuous adjustment of the laser intensity. The beam was passed through a series of apertures serving as a spatial filter and down-telescoped to give a very uniform beam profile over a diameter of about 1 mm. Typically 10–100  $\mu\text{J}$  of energy were available at the flame for the DFWM interaction.

The flame was produced by a standard welding torch (1 mm nozzle) mounted on an  $x$ - $y$  stage. Fuel mixtures were slightly rich for most of these experiments. The laser passed through a region about 3 mm above the nozzle traversing the primary reaction zone. The 1 mm diameter laser beams, crossing at an angle of  $15^\circ$ , defined an interaction volume of  $\sim 3.5$  mm maximum longitudinal extent. Although the signal is mostly generated in a distance smaller than this maximum, the steep temperature gradients in the reaction zone result in the measurement of a temperature which is a spatial average through this region. The signal beam was passed into a 1 m Czerny–Turner spectrograph (Hilger monospek 1000) equipped with a 2400 lines/mm grating and an entrance slit set at 70  $\mu\text{m}$ . Initial experiments used an intensified CCD camera (Princeton Instruments) to record the DFWM spectra. This detector provided gating to times as short as 10 ns which reduced background emission from the bright flame very effectively. However, the image intensifier on the CCD camera degraded the spectral resolution since the microchannel plate of the system effectively integrates over four adjacent pixels. As a result of this instrumental broadening much of the detail of the closely spaced  $\text{C}_2$  spectral lines could not be resolved. Subsequent experiments were performed with an unintensified camera (Princeton Instruments, Tek 512-TK B/1 chip) having a mechanical shutter which allowed a minimum exposure time of 0.1 s. The  $\text{C}_2$  Swan-band emission from the flame, which was sampled in this time interval, was enough to almost saturate the CCD camera (digital resolution of 32 000 counts). An additional shutter assembly consisting of a modified chopper wheel was used to reduce this background by a factor  $\sim 100$  to typical levels of 150 counts. Signal levels were typically between 1000 and 3000 counts, and after subtraction of the constant background level arising from flame emission, signal-to-noise ratios of 200:1 were readily achieved. A small fraction of the ML output was delivered to the spectrograph via an optical fibre and its spectrum recorded on a different part of the camera chip. The camera orientation with respect to the entrance slit was carefully adjusted to ensure that a given pixel column corresponded to the same spectral position across the entire camera chip. Thus a one-to-one correspondence was obtained between the ML spectrum and the DFWM spectrum recorded simultaneously. The diffraction grating in the ML introduces some spectral dispersion across the output laser beam. Apertures were used to minimize the effects of this spatially varying spectral content and to produce a uniform intensity profile across the beam. It was found that the



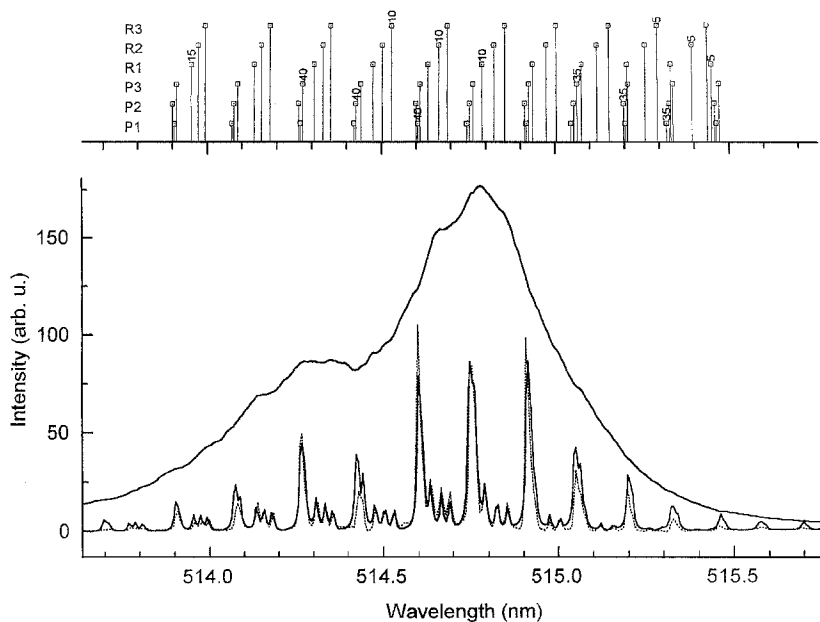
**Fig. 2.** Single shot multiplex DFWM of the bandhead in the  $d^3\Pi_g \leftarrow a^3\Pi_u(0,0)$  Swan system of  $\text{C}_2$ . The laser-intensity spectrum (*thinner line*) is superimposed on the spectrum

ML frequency spectra measured before and after the apertures differed significantly and so great care was taken to ensure that the reference beam had the same spectral content as the pump and probe beams.

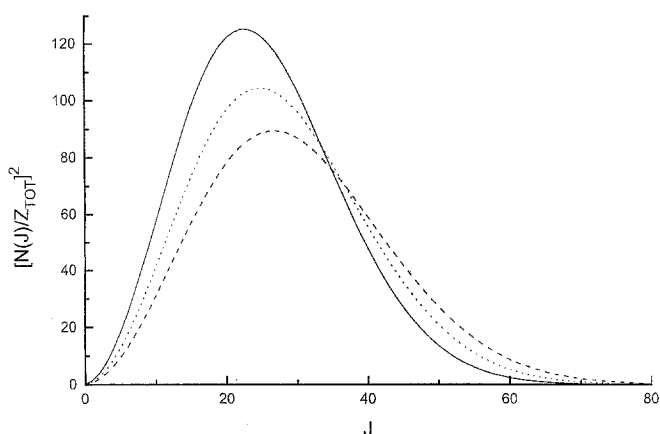
### 3 Results and discussion

A typical single-shot DFWM spectrum in the region of the bandhead in the  $d^3\Pi_g \leftarrow a^3\Pi_u(0,0)$  Swan band of  $\text{C}_2$  is shown in Fig. 2 with the “modeless” laser spectrum superimposed. This single-shot spectrum consists of over 100 individual rotational lines in the  $P$  branch. Individual single-shot spectra were very reproducible indicating good spectral stability of the “modeless” laser and the quality of the beam profiles. Owing to the heavy blending of the spectral lines near the band head and the relative insensitivity of spectra in this region to temperature changes [24] no attempt was made to derive temperatures from such spectra.

For thermometry a more temperature sensitive set of transitions was probed such as that shown in Fig. 3 where more than 60  $R$  and  $P$  branch transitions around 515 nm have been recorded in a single shot. The  $R$  branch triplets are clearly resolved demonstrating the high spectral resolution of the technique. In principle, the isolated  $R$  branch transitions could be used on their own to derive temperatures assuming a Boltzmann distribution as described in Sect. 2. However the  $R$ -branch transitions shown here exhibit only a weak temperature dependence and so a much larger range of  $J$  values is needed for accurate thermometry if only the  $R$ -branch lines are used. An alternative strategy, adopted here, uses the relative intensities of the  $R$  and  $P$  branch lines which cover a wide range of  $J$  values. Figure 4 shows the square of the population for  $F_2(J=N)$  states, normalised by the partition function, at 2500, 3000 and 3500 K. As is seen the use of both low-lying  $R$ -branch lines ( $J=7$ –11) and high-lying  $P$ -branch lines ( $J=32$ –42) results in spectra that are very sensitive to temperature changes over the range indicated. Temperature-dependent theoretical spectra including both  $R$  and  $P$  branches were synthesized and directly



**Fig. 3.** Multiplex DFWM spectrum and least-square best fit. The *upper graph* is included for spectral identification. The *spectrum* shown encompasses more than 60 lines in the *R* and *P* branches. The laser intensity spectrum is superimposed. (----) Experiment; (—) theory



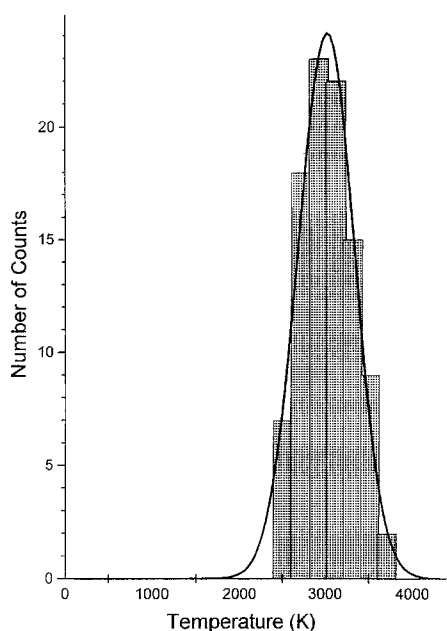
**Fig. 4.** The square of the rotational level population  $N(J)$ , where  $N(J) = (2J + 1) \exp[-BJ(J + 1)/k_B T]$ , normalised by the state sum  $Z_{\text{tot}} = \sum_r N_r$  shown for three different temperatures: (—) 2500 K; (····) 3000 K, (----) 3500 K

fitted to the experimental spectra. The transition moments were calculated using Hoenl-London factors first derived by Budó [25] assuming Hund's case *b* coupling which is rapidly approached in  $C_2$  for higher rotational quantum numbers. The theoretical spectrum was normalised by the laser power spectrum and for this purpose the power dependence of the individual transitions was measured. Although pulse energies were in the  $\mu\text{J}$  range in a laser bandwidth of more than 1 nm the DFWM spectra showed effects of partial saturation. Since the laser intensity varies significantly over the spectral range indicated different degrees of saturation apply for different transitions. However, the DFWM signal intensity  $I_s$  corresponding to individual transitions was found to scale with laser intensity  $I_L$  as  $I_L^x$  with  $0.7 \leq x \leq 1.3$ , showing that the incident laser fields were of the order of  $I_{\text{sat}}$ . It has been shown that, for a very wide range of intensities around  $I_{\text{sat}}$ , the signal

does not vary significantly from a  $\mu^4$  dependence [17]. Therefore, in the present work, a  $\mu^4$  dipole dependence and a linear dependence on laser intensity is assumed. Since the dipole moment is essentially constant for different transitions at high  $J$  values the exact dependence is not critical for thermometry in the present case. The "best fit" theoretical spectrum to the data of Fig. 3 corresponds to a temperature of 2990 K.

The spectrum shown in Fig. 3 exhibits a strong intensity alteration between successive *P*-branch transitions. In diatomic molecules  $\Lambda$ -doubling splits each rotational level into a symmetric and an antisymmetric sublevel. Since  $^{12}\text{C}_2$  has zero nuclear spin, the antisymmetric levels are forbidden and, as a result, adjacent transitions between symmetric  $\Lambda$  levels show strong "staggering" [26]. This "staggering" leads to the observed intensity alterations. Since the *P* transitions are heavily blended, in the spectral region shown, an accurate knowledge of the individual line positions is crucial for correct calculation of synthetic spectra. The observed strong alteration in intensity cannot be fully explained on the basis of the published line positions [19]. It is found that even small changes in the  $\Lambda$ -doubling parameters can cause significant changes in the shape of synthesized spectra. The error in the fit due to these imprecisions could result in a small shift of measured temperatures. Current efforts are directed at calculating accurate line positions of  $C_2$  using a computer program developed by Brown [27]. However, the temperature calculated from fitted spectra is far more sensitive to the relative scaling of *P* and *R* transitions than to the exact spectral shape of the synthetic spectrum.

Mechanical limitations of the camera shutter restricted the acquisition of large sets of single-shot data at the 10 Hz laser pulse rate. In order to protect the shutter from excessive stress the opening times were increased resulting in the acquisition of two signal pulses per exposure. Figure 5 shows a typical histogram of temperatures derived from 100 such exposures. The mean temperature



**Fig. 5.** Typical histogram of temperatures obtained from 100 multiplex DFWM spectra. The *solid line* indicates the Gaussian distribution of this data giving a mean temperature of 2993 K with a standard deviation of 325 K

is 2993 K, with a standard deviation of 320 K (10%) in good agreement with the value expected for this flame [28]. A averaged multiplex spectrum of only four laser shots could be acquired simply by using an exposure time of 0.45 s. An batch of 20 such exposures yielded temperature distributions with a standard deviation of only 3%.

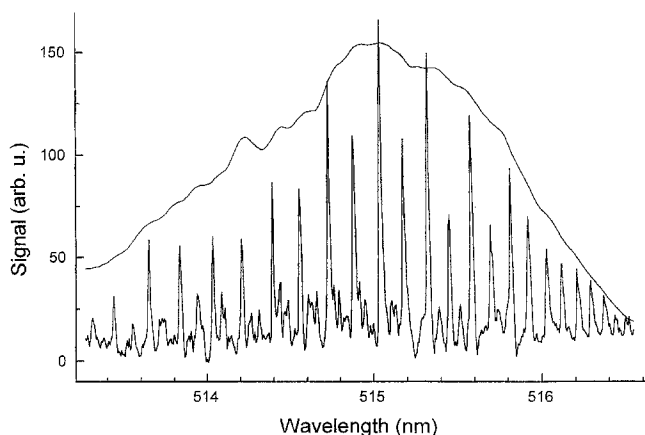
Initially a 500 mm focal length lens was used to increase signal intensities. However, a nonlinear intensity-dependent refractive index effect was observed in acetylene resulting in a large amount of light scattered into the signal beam direction. A small flow of (cold) acetylene in the interaction region was enough to seriously impair the beam profile of the focussed pump beams and to contribute to scattered light on the detector. No such effects were observed in oxygen even at much higher (more than 10 times larger) flow rates. In the flame, a slight reduction of these intensity dependent effects was observed when the fuel mixture was lean. This supported the assumption that a broad two-photon transition in unburnt acetylene in the flame was responsible for the degradation of the beam profile. DFWM in the forward scattering folded boxcars geometry was attempted by focussing three parallel beams into the interaction region [29]. This geometry has been applied successfully to detect  $C_2$  in oxy-acetylene flames using a scanning narrow linewidth laser [6]. Forward scattering experiments were attempted in the present work but were unsuccessful. In the presence of either combusting or non-combusting gas flows, noise from laser scatter increased to a level which was enough to saturate the CCD camera. This problem is attributed to the intensity dependent refractive index effects induced by the much higher beam intensities required in multiplex

DFWM. With unfocussed beams no such effects were apparent.

Previous single-shot temperature measurements using DFWM of OH, based on two-line excitation, have been conducted with conventional dye lasers. In one case, a specially designed two-wavelength laser was used [30] to probe two transitions simultaneously. In the other case, a standard dye laser having a bandwidth sufficient to span two judiciously chosen, closely spaced lines was used [11]. These experiments were affected by fluctuations of longitudinal cavity modes of the lasers. The accuracy of this technique was further limited by the use of only two lines. These problems are circumvented by use of a very broadband “modeless” laser with which a larger number of lines may be probed and problems of mode intensity fluctuations are avoided [10]. The ground-state rotational constant of OH is  $18\text{ cm}^{-1}$  compared to  $1.7\text{ cm}^{-1}$  for  $C_2$ , therefore, far fewer transitions can be excited with the same bandwidth. In  $C_2$ , the large number of rotational lines that can be excited with a ML allows accurate single-shot measurements to be performed.

As discussed in [13], the precision and accuracy of the temperatures obtained in the OH experiments were affected by the poor quality of the frequency doubled UV beams. In the present work, the fundamental of the dye laser was used resulting in a more uniform and stable beam profile. However, the grating used in the “modeless” laser causes (small) dispersion across the output beam. The effect of spectral variations across the laser beam on the multiplex DFWM signals has not yet been analysed. Owing to the inherent divergence of the laser beam it is possible that different parts of the beam have different spectral content and so the efficiency of the DFWM signal generation may vary across the spectrum leading to a systematic shift of derived temperatures. In OH experiments, these effects are aggravated when broad band radiation is produced by frequency doubling in a critically phase matched nonlinear crystal [13]. Since no frequency conversion is required to excite  $C_2$  transitions this system is ideal to study these effects. Future experiments to investigate potential problems associated with this dispersion will be conducted with a ML equipped with an interference filter to replace the grating.

To further illustrate the potential of multiplex DFWM, the bandwidth of the ML was increased by substituting a 300 lines/mm grating for the 600 lines/mm grating previously used. The bandwidth in this case exceeded 5 nm and almost the entire (0,0) band could be spanned. A typical result is shown in Fig. 6 where a spectrum containing more than 150 rotational transitions has been recorded in a single shot. Owing to the limited energy of only 45 mJ available to pump the ML, the system was not operating in the saturated amplification regime and so relatively large shot-to-shot variations were observed in the laser spectrum. Additionally, the lower spectral power density available caused a significant reduction in the observed signal-to-noise ratio. However, large bandwidths could be more reliably obtained if a more powerful pump source was employed. Spectra covering a wider range of rotational transitions will improve the accuracy of temperature measurements. If



**Fig. 6.** Single-shot multiplex spectrum with the 600 lines/mm grating replaced by a 300 lines/mm grating. The spectrum contains more than 150 individual transitions. The intensity alternation between successive peaks in the P branch is clearly visible

the laser bandwidth exceeds the separation between vibrational subbands vibrational temperatures could be derived.

#### 4 Conclusion

In conclusion, the detection of  $C_2$  in a flame by multiplex DFWM has been demonstrated and reliable temperatures derived from the recorded spectra. The use of a broadband "modeless" laser resulted in reliable and consistent single-shot data with excellent signal-to-noise ratio. The greatly improved shot to shot stability of the  $C_2$  multiplex spectra compared to previous work in OH is ascribed to improved beam quality of the laser used. The reliability and reproducibility of the data obtained justifies further efforts to improve the theory of broadband DFWM in multilevel molecular systems. The accuracy of synthetic spectra used for temperature calibration could be improved by more accurate data on the  $C_2$  molecule. Thus improvements in theoretical modelling of broadband DFWM and its application to molecular spectra may lead to further improvements in the accuracy and precision of the technique. The results reported here indicate that multiplex DFWM is a promising technique for thermometry of species in highly luminous environments.

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