Multiplex H_2 coherent anti-Stokes Raman scattering thermometry with a modeless laser

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The use of a modeless laser as the Stokes source for multiplex coherent anti-Stokes Raman scattering in molecular hydrogen is reported. The elimination of noise associated with mode competition in conventional standing wave lasers is shown to result in reliable and accurate single-shot thermometry of H_2 in a microwave-assisted diamond chemical vapor deposition plasma reactor. Single-shot temperatures are recorded with a precision of 7.3%. Possible improvements to this precision are discussed and applications of the technique for on-line process monitoring are briefly presented. © 1997 Optical Society of America

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Coherent anti-Stokes Raman scattering (CARS) has been developed into a robust diagnostic technique for combustion and plasma processes.[1] Temperature measurements may be derived from spectra obtained by scanning the frequency of a narrow bandwidth Stokes laser or, alternatively, by use of a broad bandwidth Stokes laser that allows the capture of a multiplexed spectrum from a single laser shot. Multiplex CARS[2] is now one of the most established techniques for the measurement of dynamic temperature distributions in a wide variety of plasma and combustion processes. In almost all these cases molecular nitrogen is the Raman active species used to generate the temperature-dependent spectra. However, in many plasma and some combustion environments N_2 is absent or not present in sufficient quantity to provide an adequate CARS signal. Molecular hydrogen is an attractive alternative owing to its large Raman cross section, the simplicity of its spectrum, and its presence in many plasma environments or propulsion systems.

Multiplex CARS of H_2 suffers severely from the effects of spectral noise in the outputs of the broadband lasers usually employed. This noise arises from mode competition effects in the standing wave resonators of conventional lasers. The homogeneous linewidths of H_2 Raman transitions encountered in low pressure plasmas (typically <0.005 cm^{-1})[3] are small compared to the mode spacing for typical broadband laser resonators (~ 0.01 cm^{-1}). This means that mode competition effects in the laser source can lead to enormous intensity fluctuations in corresponding CARS spectra. In particular, both amplitude and phase fluctuations contribute spectral noise that affects the precision of CARS temperature measurements.[4] A detailed comparison of spectral noise in single-shot N_2 CARS using both single-mode and multimode pump sources in combination with either a modeless or a conventional broadband Stokes laser has been reported[5] showing that the optimum combination is that of a single-mode pump laser and a modeless laser as the Stokes source. In the case of H_2 CARS, effects arising from the interplay of mode noise with the molecular response are expected to be even more pronounced because only a limited number of transitions can be excited with a given Stokes bandwidth and because of the narrow width of the individual transitions (rotational constant $B = 59$ cm^{-1} for H_2). Intensity fluctuations of individual lines in the spectrum have therefore a significant effect on the evaluated temperature. Corresponding N_2 CARS spectra are less severely affected owing to the much larger number of lines that may be probed simultaneously ($B = 2$ cm^{-1} for N_2). A detailed discussion of these problems is given in Ref. 6.

To overcome these effects, most reported thermometry applications based on H_2 CARS have been per-

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formed using either a scanning CARS arrangement (see, for example, Refs. 7–9) or by averaging a large number of multiplexed single-shot spectra when a multimode, broad bandwidth Stokes laser was used.[6,10,11]

The use of a modeless laser[12] (ML) as the Stokes source has been shown to improve the precision of single-shot N_2 CARS thermometry significantly by reducing the amount of noise imposed by the Stokes laser.[5,13] We report here the use of a ML to obtain reliable and reproducible CARS spectra of H_2 allowing accurate, single-shot, temperature measurements.

The measurements were made in a hydrogen-bearing gas mixture fed to a microwave-assisted diamond chemical vapor deposition (CVD) system. The plasma was activated by an 800-W, 2.45-GHz microwave generator. Gas flow rates of 824 sccm (standard cubic centimeters per minute) of H_2, 190 sccm of Ar, and 30 sccm of CH_4, respectively, were used maintaining a total gas pressure of 38 mbar. Details of the reaction chamber are given elsewhere.[14]

The CARS pump beams were derived from part of the 150-mJ (~7-ns pulse duration) output of a frequency-doubled Nd:YAG laser (Spectron SL4000, bandwidth ~0.9 cm^{-1}) with the residue being used to pump the ML that provided the Stokes beam. The device emits light having an essentially continuous spectrum since it does not employ a standing wave resonator. It was arranged to operate without any spectral narrowing by removing the diffraction grating from the system described in Ref. 12 and placing the end prism in line with the dye cell and the other reflecting prism. A solution of LDS 698 dye in methanol was used in the ML and in a single, transversely pumped, amplifier stage. With a total pump energy of approximately 90 mJ, the system yielded an output of approximately 6 mJ in a bandwidth of 13 nm centered at 677 nm.

Both pump and Stokes beams were spatially filtered and their beam waists and divergences matched using adjustable telescopes before being combined in a planar BOXCARS geometry.[15] The beams were focused in the reaction chamber by a 20-cm focal-length lens and the emerging beams were recollimated by a similar lens. The CARS signal was directed to a 1-m spectrograph (Hilger Monospek 1000, 2400-lines/mm grating, 100-μm entrance slit) and the CARS spectra were recorded by an intensified CCD camera (Princeton Instruments).

The amplitudes and shapes of the resonant susceptibilities $|\chi_{CARS}|$ were calculated using the CARSFIT computer code[16] that accounts for the dependence of $|\chi_{CARS}|$ on the rotational level number J, temperature, and pressure. The observed line shape is given by a convolution of $|\chi_{CARS}|$ with the pump laser line shape, and the square of this convolution is convolved with the detection system response function. In the present case, the largest contribution to the overall line shape was given by the camera response function (FWHM of 1.7 cm^{-1}). The overall line shape was found to be well approximated by a Gaussian function scaled by peak heights of $|\chi_{CARS}|$. Experimental spectra were fitted, using a least-squares minimization routine (NAG E04JAF), to theoretical spectra from a library of calculated spectra that were normalized by an averaged nonresonant CARS spectrum generated in argon at room temperature and 700-mbar pressure.

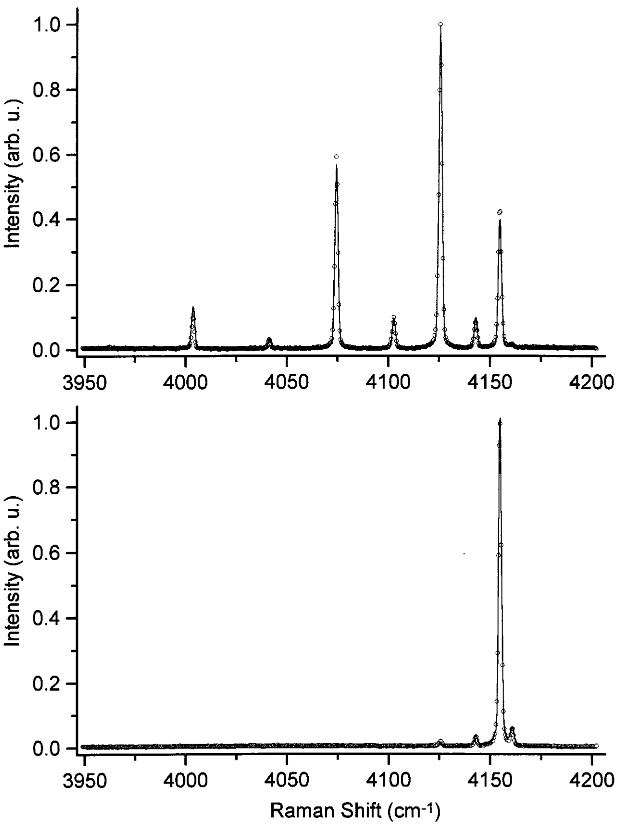

Fig. 1. Top: single-shot CARS spectrum of H_2 (circles) and theoretical fit (solid curve). The best-fit theoretical spectrum corresponds to a temperature of 2340 K. Bottom: room-temperature spectrum included for comparison.

Figure 1 shows a single-shot H_2 CARS spectrum and a best-fit theoretical spectrum corresponding to a temperature of 2340 K (top graph). Also shown is a fitted room temperature spectrum obtained in 2 Torr of pure H_2 in the reactor chamber with no microwave excitation (bottom graph). The best-fit theoretical spectrum corresponds to a temperature of 300 K in agreement with the measured laboratory value. The spectra were checked to ensure that no saturation effects were present and that the signals had the required quadratic dependence on H_2 density. The use of the BOXCARS geometry, giving a short interaction length of 1.5 mm compared to the diameter of the plasma ball (~50 mm), ensured that the measurement volume was homogeneous in temperature.

The precision of single-shot measurements is indicated by a typical histogram as shown in Fig. 2, which shows the temperature distribution obtained from a batch of 250 single-shot spectra. The mean temperature of the distribution corresponds to 2337 K.

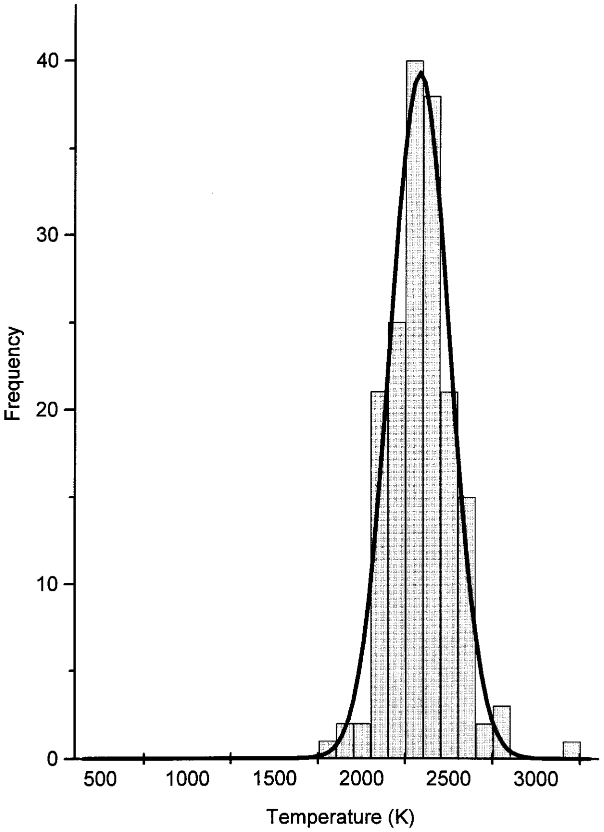

Fig. 2. Temperature distribution corresponding to 250 single-shot CARS spectra. The histogram corresponds to a most probable temperature of 2337 K with a standard deviation of 171 K. A Gaussian fit to the distribution is also shown.

This value is in good agreement with independent temperature measurements of the plasma obtained from laser-induced fluorescence scans from C_2 that were performed under similar conditions.[14] The histogram is characterized by a Gaussian distribution having a standard deviation of 171 K or 7.3%, which is significantly lower than that previously achieved by single-shot H_2 CARS thermometry.[6,17] However, it is larger than that typically achieved in conventional single-shot N_2 CARS (~4–5%). In the present case the width of the distribution is a reflection of spectral and intensity fluctuations in the ML, mode noise on the multimode Nd:YAG pump laser, and temperature fluctuations caused by instabilities in the plasma itself.

The rms spectral noise of the ML, measured as the averaged standard deviation from the mean intensity across the spectrum, was higher than optimum owing to its very wide bandwidth (~13 nm) and nonsaturation of the amplifier medium. The measured noise value of 5.3% is significantly larger than the figure of ~3% achieved in N_2 CARS studies in which a ML bandwidth of ~5 nm suffices to cover the entire spectrum.[5] Thus one can expect additional improvement over the present results by saturating the amplifier stage and by using a single-mode pump laser.

The consistency of the spectra that were obtained using the ML suggests that this system could provide accurate, real-time monitoring of temperatures in plasmas having an appreciable H_2 content. The use of quick-fit methods[18] would render the computation of temperatures from the spectra feasible within the time intervals between laser pulses at 10 Hz.

The use of a broad bandwidth modeless dye laser for multiplex H_2 CARS has been demonstrated for the first time as far as we know and has been shown to reduce significantly the fluctuations induced by laser mode noise. Use of this device has allowed the first time-resolved temperature measurements in a low pressure diamond CVD plasma using multiplex H_2 CARS. Single-shot temperatures were obtained having a standard deviation of 7.3% on batches of 250 spectra.

These results demonstrate the potential of multiplex H_2 CARS, using a modeless laser, as a tool for on-line diagnostics and plasma process monitoring. This system has been used for detailed studies of a microwave-assisted diamond CVD reactor and has allowed the temperature of the plasma to be monitored as a function of various plasma parameters such as pressure and input microwave power. The ability to make rapid, accurate, and reliable temperature measurements facilitated the study of temperature changes over a wide range of plasma parameters. The results of these studies will be reported elsewhere.[19] Application to other hostile environments such as combustion processes, for example, in which hydrogen rather than nitrogen is the majority Raman active species, can be clearly envisaged.

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