

DEGENERATE FOUR-WAVE MIXING AS A SPECTROSCOPIC PROBE OF ATMOSPHERIC PRESSURE REACTING PLASMAS.

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ABSTRACT

The applicability of degenerate four-wave mixing (DFWM) as a spectroscopic probe of atmospheric pressure reacting plasmas has been investigated. This powerful, nonlinear technique has been applied to the measurement of temperature and radical species concentrations in the boundary layer of a diamond growth substrate immersed in a flowing plasma. Results of these measurements are compared with those obtained by optical emission spectroscopy (OES), and with the predictions of a detailed numerical simulation.

INTRODUCTION

The study of atmospheric pressure plasmas relies heavily on spectroscopic diagnostics to extract important quantities of interest. For many diagnostic techniques it is quite challenging to provide useful and accurate information from such a harsh and potentially nonequilibrium environment. This paper describes the first investigation into the applicability of a powerful nonlinear spectroscopy, degenerate four-wave mixing (DFWM), to atmospheric pressure plasma chemistry. This technique has been successfully applied to static cells [1,2], combustion environments [2-4], and low pressure discharges [5], and appears to be a very promising diagnostic for thermal plasmas [6,7].

The DFWM technique utilizes three laser beams of a single wavelength interacting with the plasma to produce a fourth spatially coherent, polarized signal beam that can be collected with high efficiency, and effectively filtered from the intense plasma luminosity. This feature is perhaps the greatest advantage of DFWM over other traditional diagnostic tools of atmospheric pressure plasmas which are often disabled or corrupted by the intense background luminosity. DFWM is found to be an extremely useful nonintrusive probe of the plasma, capable of providing high spectral and spatial resolution, and permitting measurements of temperature and relative species concentrations of trace radicals under conditions in which other spectroscopic techniques fail. Since DFWM can be used to probe the ground state of electronic transitions, it is much less subject to misinterpretation as a result of nonequilibrium effects [8] than conventional techniques such as optical emission spectroscopy (OES). Measurements of vibrational and rotational temperatures, as well as relative concentration profiles for CH and C₂ radicals have been measured in the thin boundary layer of a diamond-growth substrate immersed in a flowing atmospheric pressure plasma. These results are compared with measurements obtained using OES, and found to differ as a result of the effects of plasma nonequilibrium on the OES measurements. DFWM measurements of temperature and relative species concentrations are also compared with the results of a detailed numerical simulation of the reacting plasma, and found to be in agreement.

EXPERIMENTAL FACILITY

The RF inductively coupled plasma (ICP) torch facility has been described in previous work [9,10]. The present experiments were conducted inside a water cooled quartz test section which is shown in schematic cut-away along with the plasma torch head in Figure 1. Open-ended

laser access ports, approximately 6.5 cm downstream of the nozzle exit, enable the DFWM pump and probe beams to enter and exit the reactor unhindered, and to cross at a location directly below the stagnation point of the substrate. Substrates are supported within the quartz test section in a stagnation point flow geometry by means of a water cooled holder. The substrate can be vertically translated in-situ to allow laser measurements to be made at various points through the boundary layer. Substrate temperature is monitored with a Pyro-Micro disappearing filament optical pyrometer. Reactant gases (hydrogen and methane) are premixed with the carrier gas (argon) before passage through the RF discharge.

The optical configuration for this facility is shown schematically in Figure 2. Plasma emission measurements were made using a SPEX model 1400-II 3/4 meter scanning monochromator fitted with a Hamamatsu model R1104 photomultiplier tube. Absolute intensity calibrations were obtained by means of a tungsten strip lamp, with a calibration traceable to NIST standards. Plasma emission was monitored from the freestream, 1 cm upstream of the substrate surface.

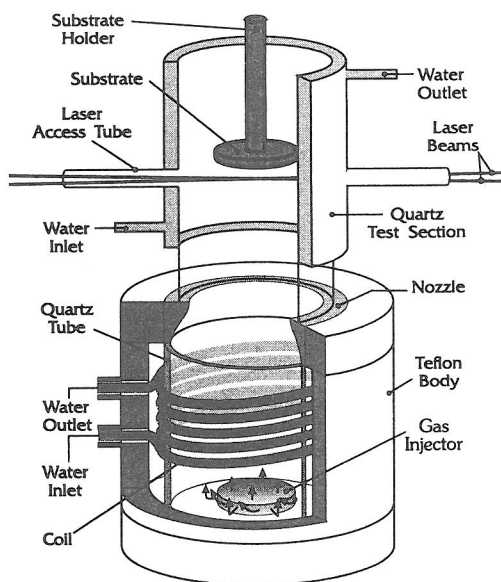


Figure 1. Schematic of RF-ICP reactor.

Plasma emission was monitored from the freestream, 1 cm upstream of the substrate surface. Laser beams

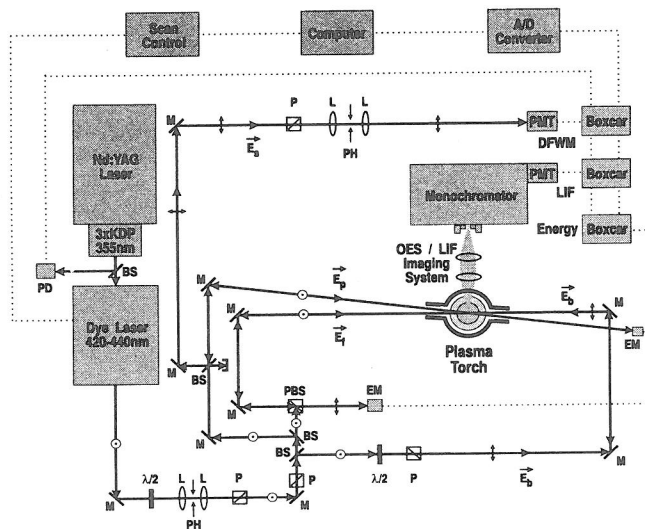


Figure 2. Schematic of facility optical setup.

for the DFWM experiments are produced using a Nd:YAG pumped dye laser system. The output of the laser is spatially filtered to improve beam quality, and reduced in intensity with a variably rotated half-wave plate, fixed polarizer combination. The beam is then split into three beams (of approximately equal energy at the test section), the backward pump beam (denoted E_b), the probe beam (denoted E_p), and the forward pump beam (denoted E_f). Polarization of the backward pump beam is rotated with a half-wave plate to be

perpendicular to the polarization of the forward pump and probe beams, thus aiding signal isolation. Beam convergence is adjusted to produce a mild focus at the mid-line of the test section, producing beam waists of approximately 300 μm diameter. The forward and backward pump beams are brought coaxial and counterpropagating through the test section laser ports, and the probe beam crosses the pump beams at a slight angle ($\approx 2.1^\circ$) directly beneath the stagnation region of the substrate. Geometric interaction length of the pump and probe beams is approximately 16 mm (parallel to the substrate surface).

The phase-conjugate signal beam (denoted E_s) is generated in the interaction region and follows the reverse path of the probe beam out of the test section. This signal beam counterpropagating along the probe beam line is separated by means of a beamsplitter, spatially filtered to reject incoherent scattering, and detected with an unfiltered photomultiplier tube. Beam energy is continuously monitored by means of two joulemeters which terminate the probe and backward pump beams.

RESULTS

The in-situ measurement of temperature and species concentration within the boundary layer of a diamond growth substrate is both challenging and very informative. Previous techniques for sensitive, spatially resolved measurements of thermal plasmas have been faced with many difficulties in implementation and interpretation due to the very nature of these plasmas. The highly luminous environment, steep gradients, and nonequilibrium behavior complicate attempts to study and model these plasmas, but are also the driving forces behind the increasing usefulness and desire to learn more of these plasmas.

The most demonstrative example of this trend is in the synthesis of diamond thin films via atmospheric pressure plasmas. Here, the high density and steep gradients (producing strong nonequilibrium) are used to produce high quality diamond films at high growth rates. The very limited understanding of this process, however, has been gleaned from careful interpretation and creative theories based on many parametric studies of diamond growth. The bulk of these data comes from ex-situ study of two "bottom-line" quantities, namely growth rate and quality (with the latter being evaluated by a number of techniques ranging from Raman scattering and morphology to thermal diffusivity). The few in-situ diagnostics (e.g. residual gas analysis, emission spectroscopy, molecular beam mass spectroscopy, absorption, etc.) have been primarily directed at low pressure growth environments (which often have additional complications compared with their atmospheric pressure counterparts), and have had some limited success [11].

In this paper, the applicability of in-situ DFWM to thermal plasmas has been investigated using the well controlled, atmospheric pressure ICP diamond growth environment as a test case. In-situ measurements of the trace radicals CH and C_2 have been performed to determine vibrational temperatures, rotational temperatures, and relative species concentration measurements (including profiles of these quantities through the reacting boundary layer above the growth substrate), and compared with the results of emission spectroscopy. In this study it was desired to make in-situ measurements during normal operation of the atmospheric pressure RF-ICP diamond synthesis reactor - with a substrate in place, and growing diamond. The conditions chosen for this preliminary study were indeed diamond growth conditions (although they were not optimized for best possible growth) and all measurements reported here were taken with the growing substrate in place. The reactor gas feed mixture was comprised of 106.5 l/min Ar, 12.0 l/min H_2 , and 0.55 l/min CH_4 premixed before introduction to the plasma torch. Calorimetric energy balance of the reactor indicates a net plasma enthalpy of 6 kW leaving the nozzle exit. The molybdenum substrate had a measured surface temperature of 1035°C.

OES measurements were made on atomic hydrogen lines, continuum emission, C_2 Swan bands, and the CH $A \leftarrow X$ bands. Absolute and relative intensity measurements of the atomic hydrogen lines indicate a freestream temperature of approximately 5600 K. It is interesting to note that the line-of-sight emission of atomic hydrogen lines changes very little as a function of distance from the substrate surface. This indicates that the majority of atomic hydrogen emission is arising from regions radially outside the boundary layer in front of the substrate, and is thus not an appropriate measure of the growth environment of the substrate. Absolute continuum measurements indicate a freestream electron density of $1.4 \times 10^{15} \text{ cm}^{-3}$, which in equilibrium would correspond to a temperature of approximately 8000 K. Vibrational temperature measurements of the C_2 $d^3\Pi_g (v=0,1,2,3) \leftarrow a^3\Pi_u (v=1,2,3,4)$ band system at near 5600 Å yield a freestream temperature of approximately 3200 K. This value is due primarily to the fact that line-of-sight radical emission measurements are dominated by the region of peak radical concentration (which for C_2 in equilibrium is approximately 3800 K), and thus temperatures derived from those measurements are biased toward that temperature. It is important to note here that unlike many flame situations, the C_2 emission and corresponding radical concentration in this experiment are *not* likely to be the result of chemiluminescent reaction. This is due to the high collision rates present at atmospheric pressure, combined with the fact that the reactor under study is chemically well downstream ($\approx 10\text{ms}$) of the region of energy addition. Thus the C_2 radical concentration and emission are expected to be very close to those prevailing under equilibrium at the gas temperature. Both CH and C_2 line-of-sight emission are found to change very little as a function of distance from the substrate (approximately a factor of three decrease from 10 mm away to < 1 mm away), indicating those emissions as well are dominated by regions radially outside the boundary layer in front of the substrate.

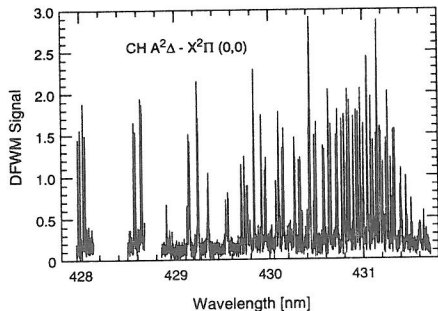


Figure 3. DFWM spectra of CH $A^2\Delta \leftarrow X^2\Pi (0,0)$.

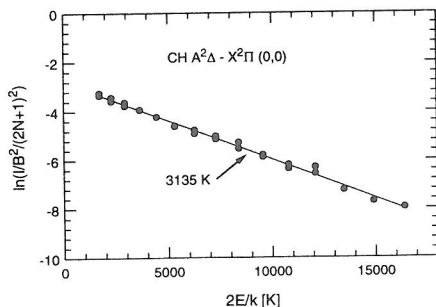


Figure 4. DFWM rotational Boltzmann plot.

In-situ DFWM measurements of the CH $A^2\Delta \leftarrow X^2\Pi (0,0)$ system near 431 nm have been performed to determine vibrational and rotational temperature profiles through the reacting boundary layer. Figure 3 shows a DFWM spectrum of this region taken with approximately 10 μJ laser beam energies. The small groups of lines to the left side of the figure are the grouped components of individual rotational lines in the R branch, while the closely spaced lines toward the right side of the figure are individual lines comprising the Q branch (the P branch is not shown). The $v''=0$ and $v''=1$ sets of individual R branch lines are closely grouped and permit determination of vibrational temperatures. The Q branch region allows fairly rapid measurements of several $v=0$ lines, thus permitting rotational temperature measurements to be made throughout the reacting boundary layer. An example of this rotational temperature determination is shown in Figure 4 where the intensity of measured Q branch lines (from $N = 6$ to 20) are plotted on a DFWM Boltzmann plot. This is shown to yield a straight line

distribution (indicating rotational equilibration) whose inverse slope indicates a rotational temperature of 3135 K.

A comparison of measured CH vibrational and rotational temperatures along the stagnation line of the substrate with values from the computational simulation are shown in Figure 5. Boundary conditions for the simulation are the DFWM measured freestream temperature of approximately 3900 K, an estimated freestream velocity of approximately 8 m/s, and the measured substrate temperature of 1035°C. We can see in Figure 5 the predicted thermal boundary layer (≈ 6 mm thick) with a steep fall off in temperature very close to the substrate. The measured CH vibrational temperatures are in close agreement with the predictions, although the loss in signal of the $v=1$ transitions in the cooler region very near the substrate prevents accurate vibrational temperature measurement for distances < 2 mm. Rotational temperatures measurements from the CH $v=0$ lines, which remain strong enough for accurate measurement closer to the substrate are in good agreement with both the measured vibrational temperatures and the computational simulation. It is possible to make rotational temperature measurements even closer to the substrate than shown in Figure 5, but for these particular experimental conditions the CH concentration in that region has dropped below approximately 2 ppm, which is our current detection limit.

Measurement of relative radical concentration is also possible within the reacting boundary layer itself, as evidenced by the results shown in Figure 6. Here, measurements of the relative CH mole fraction and vibrational temperature are compared to the results of a one-dimensional simulation [7,12] of the reacting boundary layer. In this case, at the freestream temperature of 4100 K, the CH mole fraction is approximately 20 ppm in the freestream and is predicted to first rise within the approximately 6 mm thick boundary layer (due to production) as the plasma cools toward approximately 3700 K, reaching a peak of approximately 55 ppm at 2 mm from the substrate surface, then to be destroyed as the plasma cools further on its approach to the substrate surface. We can see that the DFWM measurements of relative CH mole fraction (scaled to the peak of the predicted curve, and in agreement with the calibrated equilibrium freestream [6]) correspond closely to the predicted

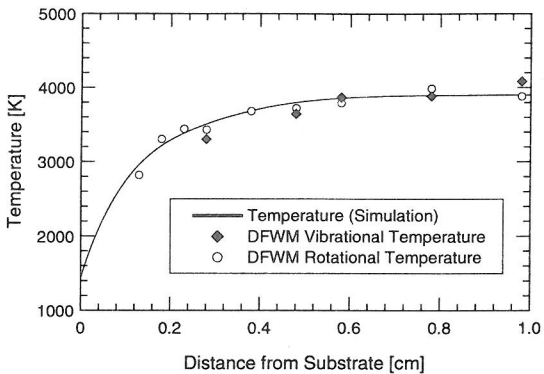


Figure 5. Measured and predicted temperature profiles.

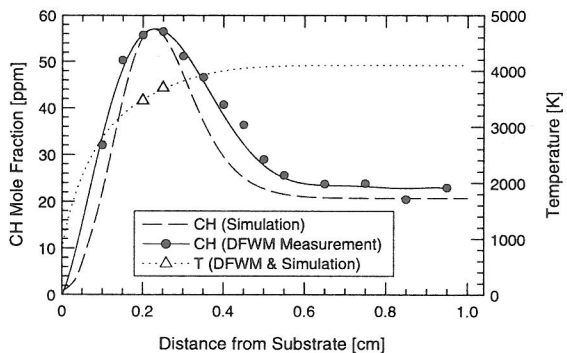


Figure 6. Measured and predicted CH concentrations.

curve in both trend and magnitude, accurately reflecting the production and destruction of CH within the boundary layer and demonstrating the ability of DFWM to probe this small, harsh reaction zone.

CONCLUSIONS

Degenerate four-wave mixing has been demonstrated as a sensitive, spatially resolved diagnostic tool for atmospheric pressure reacting plasmas. The coherent, phase-conjugate signal produced in this technique enables the rejection of intense plasma luminosity, and allows the accurate interrogation of temperature and trace (ppm level) radical concentrations within the reacting plasma. Results obtained using line-of-sight optical emission spectroscopy are found to be inaccurate and misleading due to the effects of plasma nonequilibrium and spatial averaging. DFWM measurements of vibrational and rotational temperatures, as well as relative CH radical concentrations in the reacting boundary layer of a diamond growth substrate are found to be in good agreement with model predictions.

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