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Predictions of chemical species via diode laser spectroscopy

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Abstract: A technique to predict temperature and chemical species in flames from absorbance measurement of one chemical species is presented. Predicted temperature and mole fractions of methane and water agreed well with measured and published results.

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1. Introduction

For combustion flows, the determination of temperature is extremely important for quantifying species concentrations from diode laser measurements. Such needs could be circumvented through the use of a novel prediction techniques coupled with combustion models. In non-combusting flows without temperature variations, species concentrations measured using diode laser spectroscopy (DLS) are trivially quantified using simply prepared calibration standards. However, in combusting flows, line shape variations and density corrections become large over the wide range of temperatures experienced. For real-time measurements in time-varying flows, wavelength modulation spectroscopy (WMS) provides the high sensitivity to achieve quantitative detection. But calibration issues in determining the temperature-dependence of spectroscopic parameters and response of the system to varying line-shapes become critically dependent on accurate knowledge of the temperature. While fitting absorption line shapes or making ratio measurements of line intensities can provide an estimate of local temperature, this is extremely difficult for high bandwith systems.

A generalized approach, referred herein as *Iterative Temperature with Assumed Chemistry* (ITAC), is suggested. From DLS measurements of a single major or minor species absorbance, ITAC can be utilized to quantify the measured species and to predict the other chemical species with the appropriate choice of combustion models. The approach of a conserved scalar (e.g. mixture fraction) is taken here to model the interaction between combustion and fluid dynamics in reacting flows. Chen et al. [1] have already applied ITAC to flame-vortex interactions under micro gravity conditions. In this paper, the technique is used to probe chemical species in a methane/air diffusion flame generated by a Wolfhard-Parker burner under atmospheric conditions. Methane concentration is measured and other chemical species and temperature are predicted and compared to published results.

2. Experimental setup

The diode laser spectroscopy system includes the laser system, digital signal processor (DSP) board, controller, data acquisition system and pre-amplifier [1]. The laser beam is collimated by an anti-reflection coated aspheric lens and is pointed onto a raster scanner mirror. As the mirror is rotated over an angle of about 30 degrees, the reflected laser beam hits an off-axis paraboloid reflector (OAP). The scanner mirror is positioned at the focus of this OAP so that all rays reflected by the OAP are parallel. As the beam is swept by the scanner, it tracks in parallel lines across the flame. After traversing the flame, a second OAP collects the beam and refocuses it onto a single photodetector. This optical system can scan a range of up to 4 cm. The result of this process is that data acquired sequentially in time are used to obtain spatially-resolved line-of-sight measurements across a diffusion flame. A diode laser is used to detect the nearly degenerate rotational triplet R3 A2 in the $2\nu_3$ vibrational band of methane at 1652.9 nm. The HITRAN [2] database is used to analyze the spectra. Wavelength modulation spectroscopy detection is accomplished by digitally modulating (using a modified square wave) the laser wavelength at 25 kHz and detecting the $2f$ (50 kHz) component of the photocurrent. Each spectrum of 65 points, spanning a 1.18 cm^{-1} wavelength range, are recorded in 3.0 msec. A total number of 31 positions are measured across the flame with spatial resolution of 1 mm. The DSP board controls all laser and scanner ramps, and acquires the raw data from the photodiode. These data are then $2f$ demodulated at the correct phase, normalized to the incident laser intensity and stored for subsequent download and analysis.

The flame is generated from a Wolfhard-Parker burner [7] using methane and air. The burner consists of three sections of rectangular nozzles. The center nozzle is 8 mm × 40 mm with a cold fuel exit velocity of 11 cm/s, and the side nozzles are 16 mm × 40 mm each with a cold oxidizer exit velocity of 22 cm/s. The laser beam is scanned across the width of the nozzle. Methane measurements were conducted at heights of 7, 9 and 11 mm above the nozzle. In this paper, only measurements at 9 mm above the nozzle are presented.

3. Combustion Models

The process of converting measured absorbances to mole fractions is trivial for chemical species in non-combusting flows. However, the process becomes complicated when measurements are conducted in combusting flows. In order to convert measured absorbances to mole fractions, the local temperature needs to be known accurately. Combustion models can be utilized to predict the temperature at the measurement locations. As the Damkohler number (the ratio of characteristic flow time and characteristic chemical time) approaches infinity, equilibrium chemistry dominates the reactions for which the chemical species and temperature are only a function of mixture fraction [3]. The mixture fraction is defined as the ratio of the mass originating from the fuel stream and the mass of the mixture. For finite Damkohler number, non-equilibrium chemistry dominates the reactions for which the chemical species and temperature are functions of mixture fraction and scalar dissipation rate. The scalar dissipation rate sets the molecular mixing rate between the fuel and oxidizer, and it is the instantaneous dissipation rate of the scalar energy per unit mass due to molecular diffusion in the flow.

The state relationships for the equilibrium chemistry suggest that by just knowing the mixture fraction, all the chemical species concentrations and temperature in the flame can be readily determined. On the other hand, the mixture fraction and scalar dissipation rate need to be known for non-equilibrium chemistry in order to accurately determine the chemical species concentrations and temperature. ITAC was implemented and compared using two models.

The first combustion model uses CETPC [4] to generate the equilibrium chemistry database for methane-air reaction. The peak temperature is 2225 K and the stoichiometric mixture fraction is 0.055. The second combustion model uses OPPDIF [5] and includes differential diffusion effects and chemical kinetics to generate near-equilibrium chemistry results. In the computations, the strain rate was set to as low as 2.5 s^{-1}. Simplified or full chemical kinetics can also be incorporated into the code. In this case, GRI-Mech 3.0 was used for the chemical kinetics [6]. These databases store the chemical species and temperature as a function of mixture fraction

4. ITAC

At each spatial location, absorbance measurements of the methane mole fraction is provided and analyzed asuuming (arbitrary) T=300 K at all points. In order to quantify the measurements, temperature needs to be known. The following procedures are used to correct the DLS measurements by determining the temperature iteratively: (1) Guess the mixture fraction. The corresponding mixture fraction for the initial mole fraction as determined from the data can be used as the initial guess; (2) Obtain theoretical mole fraction of methane and temperature for the guessed mixture fraction from the database; (3) Correct mole fraction of methane from DLS using the temperature obtained from the second step. The mole fraction of methane changes with temperature due to the decrease in number density, change in absorption cross section, and from line-shape effects on the WMS response; (4) Compare the methane mole fraction obtained from the database and the temperature-corrected methane mole fraction from DLS measurements. If the two values are comparable, then the correct local temperature was obtained. If not, then the the above procedures are repeated by guessing a new mole fraction and iterating.

5. Results & Conclusions

Figure 1 shows the comparison between published [7], experimental, and predicted results of methane, water, and temperature for the Wolfhard-Parker burner at 9 mm above the nozzle. Note that only measurements of methane absorbances were used with ITAC for predicting methane and water concentrations, and temperature profiles. The iterative process of ITAC guesses and refines the mixture fraction by comparing the resulting mole fraction of methane with the guessed mixture fraction and the mole fraction of methane computed from the methane absorbances with the resulting temperature for the guessed mixture fraction. The discrepancy between the measured concentration of methane

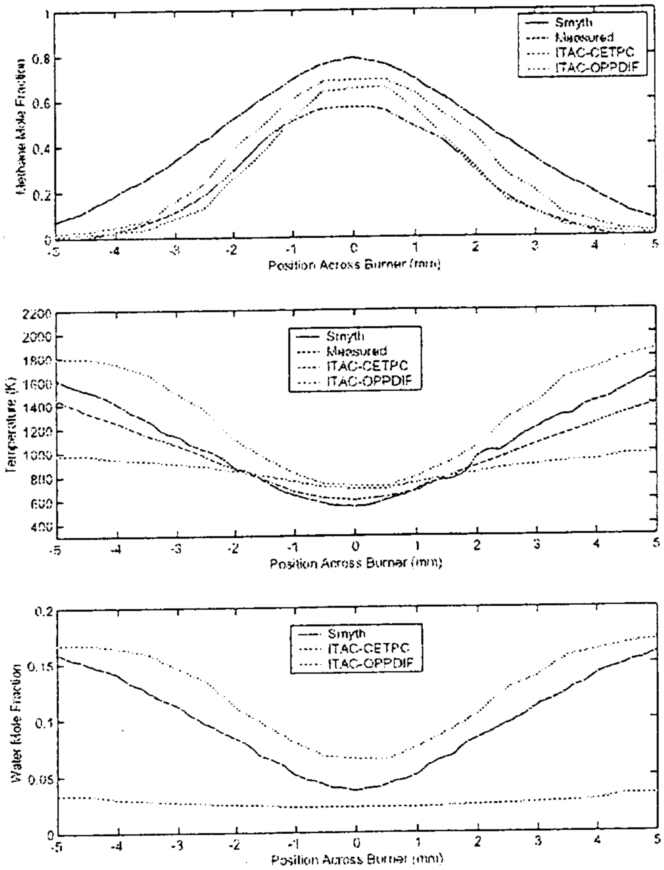

Fig. 1. Comparisons between measured, predicted, and published results of methane concentrations (top), temperature (middle), and water concentrations (bottom) in a methane/air diffusion flame of a Wolfhard-Parker burner at 9 mm above the nozzle.

(using measured temperature for quantifying the absorbances) and the published results of Smyth et al. [7] is possibly due to the incomplete response of the laser to a modified square wave modulation. Concentrations of methane are well predicted by the two combustion models. However, the temperature distribution and water concentrations are not well predicted by CETPC. Better agreement between predictions and measurements is seen with the near-equilibrium model of OPPDIF. The comparisons further suggest that non-equilibrium chemistry models will need to be implemented to improve predictions of the major species and temperature profile, especially the minor species; this will entail the measurement of a radical species (e.g. OH).

The method of ITAC provides a way to predict combustion reactants, products and temperature from the absorbance measurements of one (e.g. CH_4, H_2O, or CO_2) or two species (e.g. CH_4 and OH). ITAC eliminates the need to directly measure temperature in order to quantify DLS measurements, and may prove to be a very powerful tool in monitoring combustion by improving efficiency and reducing the emissions of pollutants.

6. References

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