Chemiluminescence-based multivariate sensing of local equivalence ratios in premixed atmospheric methane-air flames

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Abstract

Chemiluminescence emissions from OH^*, CH^*, C_2^*, and CO_2^* formed within the reaction zone of premixed flames depend upon the fuel-air equivalence ratio in the burning mixture. In the present paper, a new partial least square regression (PLS-R) based multivariate sensing methodology is investigated and compared with an OH^*/CH^* intensity ratio-based calibration model for sensing equivalence ratio in atmospheric methane-air premixed flames. Five replications of spectral data at nine different equivalence ratios ranging from 0.73 to 1.48 were used in the calibration of both models. During model development, the PLS-R model was initially validated with the calibration data set using the leave-one-out cross validation technique. Since the PLS-R model used the entire raw spectral intensities, it did not need the nonlinear background subtraction of CO_2^* emission that is required for typical OH^*/CH^* intensity ratio calibrations. An unbiased spectral data set (not used in the PLS-R model development), for 28 different equivalence ratio conditions ranging from 0.71 to 1.67, was used to predict equivalence ratios using the PLS-R and the intensity ratio calibration models. It was found that the

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equivalence ratios predicted with the PLS-R based multivariate calibration model matched the experimentally measured equivalence ratios within 7 percent; whereas, the OH^*/CH^* intensity ratio calibration grossly underpredicted equivalence ratios in comparison to measured equivalence ratios, especially under rich conditions ($\varphi > 1.2$). The practical implications of the chemiluminescence-based multivariate equivalence ratio sensing methodology are also discussed.

Keywords: chemiluminescence, equivalence ratio, premixed combustion, multivariate calibration, PLS-R, cross validation, OH, CH, C_2, intensity ratio, background subtraction

Nomenclature:

LOOCV	leave-one-out cross validation
PCs	principal components
PLS-R	partial least-square regression
RMS	root mean square
RMSEC	root mean square error in calibration
RMSEP	root mean square error in prediction

1. Introduction

Real time measurement of local and global fuel-air equivalence ratios (φ) is essential for monitoring and closed-loop control of premixed combustion systems. Pollutant emissions such as oxides of nitrogen (NO_x), carbon monoxide (CO), unburned hydrocarbons (HC), and particulate matter (PM) can be reduced by controlling fuel-air equivalence ratios [1-3]. Precise control of equivalence ratio can also help in preventing serious accidents in gas turbines such as blow-off, flashback due to pressure waves, or damage to the combustor due to combustion oscillations as these turbines operate close to the lean limit [3-4]. In internal combustion (IC) engines, advanced combustion strategies such as homogeneous charge compression ignition (HCCI) [5], low temperature combustion [6], and direct injection spark ignition [7] utilize premixed or partially premixed combustion modes to simultaneously improve engine efficiencies and reduce pollutant emissions. To achieve controlled premixed or partially premixed combustion in IC engines, the real-time measurement and closed-loop control of in-cylinder local equivalence ratios are desirable. The present work is an attempt to utilize natural chemiluminescence emissions to diagnose equivalence ratios in premixed atmospheric methane-air flames with two different sensing methodologies: (1) a whole-spectrum multivariate calibration model and (2) an OH^*/CH^* peak intensity ratio calibration model.

Chemiluminescence emissions from OH^*, CH^*, and C_2^* formed within the reaction zone of premixed flames depend upon the air-fuel ratio in the burning mixture [8-10]. Easy, nonintrusive experimental detection of chemiluminescence coupled with fast response times provides a convenient approach for equivalence ratio determination. Many researchers have investigated the variations in OH^*, CH^*, and C_2^* intensity ratios with equivalence ratio [11-13]. For example, Docquier et al. [11] studied the effect of pressure on OH^*, CH^*, and C_2^* chemiluminescence intensity in methane-air premixed flames. They found a strong correlation between the chemiluminescence signal and pressure and suggested the need for a multi-wavelength sensor for direct monitoring of equivalence ratio. Hardalupas et al. [2] showed that in natural-gas-fuelled, premixed, counter-flow flames OH^*/CH^* is independent of strain rate and that C_2^*/CH^* and C_2^*/OH^* show a strong dependence on strain rate. In a recent study [14], it was shown that in premixed counter-flow methanol and ethanol flames, OH^*/CH^* intensity ratio also shows dependence on strain rate. The aforementioned studies clearly indicate the need for the development of a robust sensing methodology that is applicable over a range of combustion conditions.

Many approaches have being employed for sensing equivalence ratios from chemiluminescence spectra [15]. Muruganandam et al. [3] and Hardalupas et al. [16] used the peak intensity ratio of OH^*/CH^* for sensing equivalence ratio in combustors fueled with natural gas. Artificial intelligence-based data analysis techniques have also been explored for monitoring as well as controling combustion processes [17]. Recently, Ballester et al. [18] applied the artificial neural network technique on chemiluminiscence spectra obtained from combustion of natural gas blended with hydrogen in a swirl combustor for monitoring equivalence ratios.

All of the previous studies show that the chemiluminescence emissions of OH^*, CH^*, C_2^*, and CO_2^* (the nonlinear continuous background) from the reaction zone depends on the equivalence ratio. In this work, a new multi-wavelength (multivariate) sensing methodology is proposed for the determination of equivalence ratios in premixed methane-air flames. Most of the previously reported work did not consider the whole spectrum approach. A model based on multivariate statistics is relevant for a two-dimensional (X, Y variables) data set, where the response Y-variable (equivalence ratio) depends on several explanatory X-variables (spectral wavelengths). A wide chemiluminescence spectrum (250 – 650 nm) was used to develop the multivariate calibration model. This approach ensures that the spectral intensity variations from all the excited species within the measured wavelength range are used in the development of the multivariate calibration model. The experimental results presented in this paper demonstrate that the multivariate calibration model can differentiate fuel-rich, fuel-lean, and stoichiometric premixed flames. A partial least square regression (PLS-R) based multivariate calibration model is developed and it is shown that the PLS-R model successfully predicts the equivalence ratios within the developed calibration range.

2. Specific Objectives

The specific objectives of the present work are

1. To develop a multi-wavelength sensing methodology for equivalence ratio estimation and monitoring in premixed atmospheric methane-air flames.
2. To evaluate the predictive capability of the developed multivariate calibration model and compare its performance with an OH^*/CH^* intensity ratio calibration model over a range of equivalence ratios.

3. Experimental Setup

A rectangular slot burner (length: 11.2 cm, width: 0.55 cm, and height: 26 cm) was used to generate the atmospheric, premixed methane-air flames used in this study. Fuel (99.97%-pure methane) and oxidizer (breathing grade air) were mixed at room temperature, prior to entering the slot burner from the bottom end. Correlated rotameters (±2% accuracy full scale) were used to measure the flow rates of methane and air. A schematic diagram of the experimental setup is shown in Fig. 1. To cut-off fuel supply to the burner in case of an emergency; a safety shutdown switch was used in the fuel line as shown in Fig. 1. A flash arrester was also attached to the fuel cylinder as a safety precaution.

Flame equivalence ratios were calculated from the volume flow rates of fuel and air measured with the rotameters and the measured air and fuel pressures (±1% accuracy of full scale) at the outlet of the rotameters. Both fuel and air at the rotameter outlets were assumed to be at ambient temperature (298 K) and the ideal gas equation of state was used to obtain the respective mass flow rates. The equivalence ratio was defined as follows:

$$Equivalence\ ratio(\varphi) = \frac{AFR_s}{AFR_a} \tag{1}$$

where, AFR_s is the stoichiometric mass-based air-fuel ratio (17.16 for methane-air combustion), and AFR_a is the actual mass-based air-fuel ratio computed from measured fuel and air mass flow rates.

The uncertainty of the measured equivalence ratios in this study was between 3 to 5 percent. The uncertainty was estimated using the following equation [19]:

$$\frac{{U_\varphi}^2}{\varphi^2} = \left(\frac{V_f}{\varphi}\frac{\partial\varphi}{\partial V_f}\right)^2\left(\frac{U_{V_f}}{V_f}\right)^2 + \left(\frac{V_a}{\varphi}\frac{\partial\varphi}{\partial V_a}\right)^2\left(\frac{U_{V_a}}{V_a}\right)^2 + \left(\frac{P_f}{\varphi}\frac{\partial\varphi}{\partial P_f}\right)^2\left(\frac{U_{P_f}}{P_f}\right)^2 + \left(\frac{P_a}{\varphi}\frac{\partial\varphi}{\partial P_a}\right)^2\left(\frac{U_{P_a}}{P_a}\right)^2 \tag{2}$$

where, φ is equivalence ratio; V_f and V_a are fuel and air volume flow rates respectively; P_f and P_a are the pressures of fuel and air at the outlets of the respective flow meters; U_φ, U_{vf}, U_{va}, U_{Pf}, and U_{Pa} are the uncertainties associated with φ, V_f, V_a, P_f and P_a, respectively.

All optical measurements were performed approximately 2 mm above the burner edge. A fused silica, plano-convex, spherical lens with 10 cm focal length and 1.27 cm diameter focused at the center of the burner was used to collect the chemiluminescence spectra. The collected optical signal was coupled to the single end of a bifurcated optical fiber (Ocean Optics, QBIF400-UV-VIS). One of the bifurcated ends of the optical fiber was connected to an Ocean Optics USB 2000 spectrometer (600 grooves/mm grating) with a spectral resolution of 3.8 nm (full-width half-maximum) to record the chemiluminescence emission spectra. The other end was used to locate spatial position in the flame by sending a separate laser beam through it before the experimental measurements were performed. This end was closed while recording the chemiluminescence spectra. Each spectrum was acquired with a 25 ms exposure time and each recorded spectrum was an average of 20 accumulated spectra. A total of ten such averaged spectra were recorded for each equivalence ratio condition. It is well known that the chemiluminescence emissions are superimposed on the dark current background spectrum. Hence, the dark current background was also collected for each experimental condition by blocking the natural flame chemiluminescence emissions. The experiments were replicated five times in the course of three days.

4. Data Analysis

Two separate analyses were performed with the recorded chemiluminescence spectra: (1) intensity ratio analysis, and (2) multivariate data analysis. A MATLAB code was written for processing the chemiluminescence data. In the first step, the dark current background was subtracted from the raw spectra and the processed spectra were saved for the multivariate data analysis (described below). In the second step, the nonlinear background emissions were subtracted from the dark current background-subtracted spectra and the OH^*, CH^*, and C_2^* peak intensities were saved for the intensity ratio analysis. The following procedure was adopted for generation of the dark current nonlinear background. After selecting the 250-650 nm spectral region, the spectral peaks of OH^*, CH^*, and C_2^* were filtered from the spectrum. Using the rest of the spectrum, an n^{th} order polynomial (where n depended on the nonlinear background that varied with equivalence ratio) was generated by minimizing the root mean square (RMS) of error between the spectral intensity and the generated background.

The multivariate data analysis was performed using The Unscrambler® version 9.7 (CAMO, Corvallis, OR, USA). A detailed method of performing multivariate data analysis can be found elsewhere [20-21]; however, a brief description of the method is given below. Multivariate data analysis can provide important information if the variation of any analytical parameter is correlated with more than one variable. In the present case, the variation of equivalence ratio can be correlated with the variation of spectral intensities associated with various chemical species (i.e., OH^*, CH^*, C_2^*, and CO_2^*). The key difference between the intensity ratio analysis and the multivariate data analysis lies in the inclusion of the nonlinear background (associated with CO_2^* emissions) in the latter for developing the calibration model. Therefore, multivariate data analysis, as will be shown later, can provide a more robust calibration model compared to the intensity ratio method for sensing applications. The partial least squares regression (PLS-R) approach [20] was used to develop the multivariate calibration model for prediction of equivalence ratios. The inputs to the multivariate calibration model were the chemiluminescence spectra at different equivalence ratios. The PLS-R relates variations in an analytical parameter (i.e., equivalence ratio) with variations in several explanatory variables (i.e., spectral intensities). Chemiluminescence intensities from the entire spectral range of interest (i.e., 250-650 nm) were considered as the explanatory variables. Initially, the spectral data were stored in an “X matrix” and the equivalence ratio data (calculated from the measured fuel and air mass flow rates) were stored in a “Y matrix.” In the X matrix, chemiluminescence intensities in the 250-650 nm spectral range at each equivalence ratio condition were stored in each row. Equivalence ratios were stored in the corresponding row in the Y matrix, which was essentially a column vector. The PLS-R determines the directions of maximum variations in the X matrix by simultaneously using variations in the X and Y matrices. These directions of variations are indicated by the principal components (PCs), with the first principal component (PC1) indicating the direction of maximum variations in the entire data set, the second principal component (PC2) indicating the next significant direction of variations, and so on. Subsequently, the spectral data were linearly regressed on the obtained PCs to develop the multivariate calibration model. While PLS-R provides a reasonable multivariate calibration with spectroscopic data, it also has a tendency toward over-fitting the available data. Therefore, it is important to analyze the “one-vector loading-weight plot” (the variation of the “loading weight” with the spectral wavelength), which is explained in detail in Section 5.2. Additional details regarding the PLS-R approach used in the present work are available in Ref. [20].

Full cross-validation, based on the leave-one-out cross validation (LOOCV) methodology, was used to validate the calibration model. In the LOOCV method, the spectral data for one equivalence ratio was left out for validation while the rest of the spectral data set was used for developing the calibration model. This validation process (LOOCV) was then repeated for each equivalence ratio in the entire data set [20]. After the LOOCV was performed on the developed calibration model, the predictive capability of the model was further tested using an unknown data set.

5. Results and Discussion

In this section, the chemiluminescence spectra at different equivalence ratios and peak intensities for OH^*, CH^*, and C_2^* are discussed first. Subsequently, results from both the intensity ratio calibration model as well as the multivariate calibration model are presented and discussed. Predicted equivalence ratios are compared to measured equivalence ratios for both models and the relative benefits of the multivariate calibration model are described.

Equivalence ratios ranging from 0.73 to 1.48 were considered in this study for the development of both the intensity ratio and multivariate calibration models. All equivalence ratios considered in the development of the calibration models are given in Table 1. The number of replications was selected after close observation of the flame chemiluminescence spectra for five days, with two recordings taken every day. A spectral range of 250-650 nm was used in this study as the range covers most of the chemiluminescence emissions from all the species of interest. The signal-to-noise ratio (SNR) in these measurements was different for various spectral peaks at different equivalence ratios. However, the minimum SNR of the measurements was calculated by determining the SNR of the OH^* peak at rich equivalence ratios (OH^* will have the minimum peak intensity among all spectral peaks for CH^*, OH^*, and C_2^* at rich conditions). Therefore, for these measurements, the minimum SNR was determined as the ratio of the difference between the OH^* peak intensity and the background to the square root of the background. The background is determined from the average spectral intensity in the 200-250 nm range where the chemiluminescence signal is absent. For the richest equivalence ratio examined in this study (φ = 1.48), the minimum SNR for the OH^* spectral peak at 309 nm (with a 25 ms exposure time and 20 spectra accumulations) was 18.

Figure 2 shows chemiluminescence spectra acquired at various equivalence ratios in the spectral range of interest. All the three spectra shown in Figure 2 are plotted on the same scale. Hence, the spectral intensities can be compared directly. It can be observed from Fig. 2 that along with the spectral peaks of OH^*, CH^*, and C_2^*, the nonlinear background (which is primarily due to CO_2^*) varied with equivalence ratio. Particularly at φ = 1.48, all the spectral peak intensities are reduced because of suppression in the nonlinear background. This can be associated with lower production of CO_2 in rich flames, where the presence of excess fuel (compared to oxidizer) favors the partial oxidation of some of the fuel into CO rather than CO_2. These observations support the inclusion of the nonlinear background in addition to the OH^*, CH^* and C_2^* spectral peaks in the sensing of equivalence ratios, especially in rich premixed flames.

Figure 3 shows the variation of OH^*, CH^*, and C_2^* chemiluminescence peak intensities as equivalence ratio was increased from a lean condition (φ = 0.78) to a near-stoichiometric condition (φ = 0.97), and then to a rich condition (φ = 1.48). To obtain the spectral peak intensity, the nonlinear background was subtracted from the spectrum by the method described in Section 4. It can be observed from Fig. 3 that the OH^* peak intensity, while significantly high for lean equivalence ratios (due to the abundance of OH radicals), was relatively low in comparison to the CH^* and C_2^* chemiluminescence peak intensities for rich flames. Also, the spectral peak of C_2^* shows more variations with equivalence ratio in comparison with OH^*, and CH^* spectral peak intensities. For example, the C_2^* peak intensities first increased when the equivalence ratio was increased from $\varphi = 0.78$ to $\varphi = 0.97$ but decreased to a lower value at the richest condition of $\varphi = 1.48$. It is also evident from Fig. 3 that the CH^* spectral peak intensities showed a similar behavior with equivalence ratio but the magnitude of the CH^* variations were much smaller than the C_2^* variations.

5.1 Intensity Ratio Calibration

In the literature, many researchers have employed the OH^*/CH^* peak intensity ratio as a metric for sensing equivalence ratios. As a first step in the development of the intensity ratio calibration model, the variations of the OH^*/CH^* chemiluminescence intensity ratios with equivalence ratio are shown in Fig. 4 along with data from Kojima et al. [13], who did similar studies but used Cassegrain optics instead for collecting the chemiluminescence spectra. As evident from Fig. 4, the general behavior of the OH^*/CH^* data in the present work is similar to previously reported results [3, 13, 16]. However, despite the similarity of the general trends, comparison of the present data with those from Kojima et al shows significant differences in the absolute magnitudes of the OH^*/CH^* intensity ratios. This can be attributed to the difference in the detection efficiencies of the spectrometers used in the present study and in the study of Kojima et al. Also, since Kojima et al used Cassegrain optics for the collection of highly resolved optical signal with better collection efficiencies, their peak intensities could have been higher. In Fig. 4, the increasing trend of OH^*/CH^* intensity ratio with decreasing equivalence ratio is associated with the high OH* production for lean equivalence ratios (due to excess air) [22]. The standard deviations shown with the data points for the present study were calculated based on the experimental results of five replications.

A three-parameter exponential decay curve was fitted to the calibration data. The equation of the best-fitted curve for the OH*/CH* intensity ratios is given below:

$$\frac{OH^*}{CH^*} = 0.37 + 594.84\exp(-8.91\varphi) \tag{3}$$

As given in Fig. 4, the R^2 (goodness of fit) of the fitted curve was 0.97. Root mean square error in calibration (RMSEC), which is another measure of the overall goodness of fit of the OH*/CH* intensity ratio calibration model, needs to be carefully studied during model development. The calculated RMSEC for the OH*/CH* intensity ratio analysis was 0.05. The RMSEC for any calibration model is defined below:

$$RMSEC = \sqrt{\frac{\sum_{i=1}^{n}(Y_i^p - Y_i^c)^2}{n}} \tag{4}$$

where, Y^c is the dependent variable data (intensity ratio in this case) used in the development of the calibration, Y^p is the predicted dependent variable data (again, intensity ratio here) by using the developed OH*/CH* intensity ratio calibration model (the exponential decay equation), and n is the number of equivalence ratios used in developing the calibration model.

5.2 Multivariate Calibration

A PLS-R based multivariate calibration model was developed for sensing equivalence ratios in premixed methane-air flames. In this process, the multivariate model was first developed and calibrated with an initial data set consisting of chemiluminescence spectra at different equivalence ratios and later its equivalence ratio prediction capabilities were validated with an unknown spectral data set. In the model development phase, the PLS-R based regression was performed on spectra collected at nine different equivalence ratios in the range of 0.73 to 1.48 with five replications at each equivalence ratio. The equivalence ratios used in the development of the multivariate calibration model were calculated from measured fuel and air mass flow rates. Data from the forty-five spectra were processed for developing the multivariate calibration model. As mentioned before, a whole spectrum approach was used in developing the multivariate calibration model. In this approach, the entire spectrum in the spectral range of interest (including the nonlinear background) was used to develop the calibration model. This method helped in investigating the importance of the nonlinear background vis-à-vis the predictive capabilities of the calibration model and also to ascertain if the nonlinear background showed any variations with equivalence ratio.

As discussed in Section 4, the PLS-R determines the directions of maximum variations in the X matrix (each row of X has the spectral intensities over the entire range of wavelengths for a given equivalence ratio) by simultaneously using variations in the X and Y matrices (where the Y matrix is a column vector storing the corresponding measured equivalence ratios). Since the PCs indicate the directions of variations in the data set, the number of PCs included in the development of the multivariate calibration model is very important [20]. To understand how many PCs are needed for the development of an accurate calibration model, it is useful to examine the residual validation variance for the developed calibration model as the number of PCs used for model development is increased. The residual validation variance for Y (equivalence ratio in the present case) is a measure of how well the model will perform in predictions with a similar but unknown X-data set [20]. In other words, the smaller the residual variance, the better the model will perform in predictions with an unknown X-data set and vice versa. For the present X-data set (with LOOCV validation), the residual validation Y-variance for the PLS-R based model is shown as a function of the number of PCs in Fig. 5. As evident from this figure, the residual variance decreases sharply as the number of PCs is increased from 0 to 3 and then remains constant (near zero) as the number of PCs is increased beyond 3 (up to a maximum of 20). Thus, Fig. 5 clearly establishes that it is sufficient to employ only three PCs in the development of the multivariate calibration model. If additional PCs are used, then no additional benefits are realized in the calibration model. On the other hand, if four or more PCs are used in the model development for the present data set, then the model may attempt to over-fit the available X-data (and result in modeling “noise”) instead of accurately capturing the actual variations in the X-data set; therefore, the prediction accuracy of the multivariate calibration model could potentially be compromised.

Figure 6 shows the predicted equivalence ratios obtained from the multivariate calibration model using the calibration data set versus the measured equivalence ratios. As mentioned above, the multivariate calibration model was developed with three PCs. In other words, the calibration model used three directions of variations in the original spectral data matrix to explain the variations of the chemiluminescence spectra with equivalence ratios. The measured equivalence ratios in Fig. 6 refer to the equivalence ratios that were calculated from the measured fuel and air mass flow rates, i.e., the equivalence ratios in the Y-matrix. In a comparison plot such as Fig. 6, a perfect calibration model would ensure that all of the data points in Fig. 6 lie on the 45-degree line (i.e., predicted equivalence ratios will be exactly equal to the measured equivalence ratios at all conditions). The high R^2 value (goodness of fit) for the data points in Fig. 6 indicates good fidelity in the multivariate calibration model. Compared to the OH^*/CH^* intensity ratio calibration ($R^2 = 0.97$), it is evident that the R^2 improved for the multivariate calibration model to 0.99. During the development of any calibration model, minimizing the RMSEC is very important [20]. Both the RMSEC and the root mean square error in prediction (RMSEP) of the multivariate calibration model (with LOOCV validation) were evaluated using an equation similar to Equation 4. As shown in Fig. 6, both the RMSEC and RMSEP for the multivariate calibration model were 0.02 (which was equal to the minimum uncertainty in the equivalence ratio measurements); by comparison, the RMSEC value for the OH^*/CH^* intensity ratio calibration model was 0.05. Despite these favorable indications for the multivariate calibration model, the final test of this model will be its ability to predict equivalence ratios in an unknown spectral data set. The outcomes of this test for both the multivariate calibration and the intensity ratio calibration are discussed in Section 5.3.

The “loading-weight” plot is another very important plot that should be analyzed while developing multivariate calibration models with spectroscopic data. The loading-weight provides information on the extent to which each explanatory variable (i.e., each spectral wavelength in the present scenario) has contributed in explaining the analytical parameter (equivalence ratio) along each PC in the multivariate calibration model [20]. Figure 7 shows the variation of loading weights with wavelength along each PC (i.e., “one-vector loading-weight” plot) for the developed multivariate calibration model.

Wavelengths with large (non-zero) loading-weights along a particular PC exert more influence on the developed multivariate calibration model compared to others. In other words, a PLS-R based multivariate calibration model may yield inaccurate (or even completely false) results if it does not have significant contributions from the spectral wavelengths that are known to be important in a given situation. For example, in the present case, it is well established that the spectral peak intensities of OH^*, CH^*, and C_2^* vary significantly with equivalence ratio (see Fig. 3); in fact, this was the foundation on which the OH^*/CH^* intensity ratio calibration discussed above was developed. Therefore, during the development of the PLS-R based multivariate calibration model, it may be expected that the one-vector loading-weight plot must show relatively large loading-weights at wavelengths corresponding to the spectral peaks of interest (OH^*, CH^*, and C_2^*). Otherwise, the developed multivariate calibration may not explain the variations in equivalence ratios correctly. In fact, it is quite evident from Fig. 7 that, along PC1, the spectral wavelengths corresponding to OH^*, CH^*, and C_2^* show non-zero loading-weights. Moreover, the nonlinear background (especially between 300 and 500 nm) also shows non-zero loading-weights. Hence, along PC1, the spectral information from the nonlinear background (due to CO_2^* chemiluminescence emissions) as well as from the OH^*, CH^*, C_2^* chemiluminescence emissions was used to model the variations in equivalence ratios. The loading-weights along PC2 also show similar trends but with relatively larger loading-weights at wavelengths corresponding to OH^*, CH^*, and C_2^* spectral peak intensities and lower contributions from the nonlinear background compared to PC1. Finally, along PC3, the loading-weight curve shows that only OH^*, CH^*, and C_2^* spectral peaks were used in the development of the PLS-R based multivariate calibration model, with minimal contribution from the nonlinear background. In summary, the loading-weight trends in Fig. 7 clearly establish that while the OH^*, CH^*, and C_2^* spectral peak intensities were certainly very important contributors, the nonlinear CO_2^* background also played a non-trivial part in the development of the PLS-R based multivariate calibration model.

5.3 Prediction of Equivalence Ratios from Unknown Spectral Data Set

The predictive power of the OH^*/CH^* intensity ratio and multivariate calibration models developed in Sections 5.1 and 5.2, respectively, were evaluated using an unknown, unbiased spectral data set for twenty-eight (28) different equivalence ratios between 0.71 and 1.67. This data set was taken independently after developing the two calibration models and was not used either as a training or validation data set for the LOOCV methodology used to develop the PLS-R based multivariate calibration model. The predicted equivalence ratios from the unknown unbiased spectral data are shown in Fig. 8 (a) for the OH^*/CH^* intensity ratio calibration model and in Fig. 8 (b) for the multivariate calibration model. In each of these figures, two sets of data are presented: open circles represent equivalence ratio conditions that were included in the model development and filled circles represent equivalence ratio conditions that were not included in model development. The 45 degree line (indicating perfect calibration) and the uncertainty bands for measured equivalence ratios are also shown in both figures. The uncertainty at each equivalence ratio was calculated using Equation 2 and the errors associated with the volume flow rate and pressure measurements. Comparing Figs. 8 (a) and 8 (b), it is evident that the prediction results of the PLS-R based calibration model are better than the OH^*/CH^* intensity ratio model. The performance of the OH^*/CH^* intensity ratio model was poor especially for rich equivalence ratios and for φ values not used in the original calibration. The poor predictive capability of the OH^*/CH^* intensity ratio model at rich conditions was also observed by Hardalupas et al. in their work reported in Ref. [16]. The reasons for this trend may be associated with lower OH^* peak intensities and a relatively low change in the OH^*/CH^* intensity ratio with changing φ for rich flames. On the other hand, PLS-R based multivariate calibration yielded better predictions even at rich equivalence ratios, ostensibly due to the fact that additional spectral information from other species (C_2^* and CO_2^*) were included in the development of the multivariate calibration model. Additional support for this hypothesis (i.e., improvement of multivariate PLS-R predictions due to the inclusion of C_2^* and CO_2^* spectral information) is found qualitatively in Figs. 2 and 3. In Fig. 2, it can be seen that the nonlinear background (due to CO_2^* chemiluminescence) changes significantly with equivalence ratio. For example, for $\varphi = 1.48$, the nonlinear background is suppressed probably due to partial fuel oxidation, which reduces CO_2 production, and therefore, chemiluminescence emissions from CO_2^*. In addition, for rich conditions (as shown in Fig. 3), the C_2^* spectral peaks vary more significantly with equivalence ratio compared to the OH^* and CH^* peaks. Therefore, it may be argued that one reason for the better performance of the multivariate calibration model compared to the OH^*/CH^* intensity ratio model may be the inclusion of the C_2^* and CO_2^* chemiluminescence.

5.4 Discussion of the Practical Implications of the Present Work

The proposed chemiluminescence-based sensing methodology has several practical advantages as well as some potential issues. A significant advantage of the multivariate calibration methodology over the OH^*/CH^* intensity ratio approach for equivalence ratio sensing is the removal of the need to perform nonlinear background subtraction from the raw measured spectra. This is especially important because nonlinear background subtraction, if performed without adequate care, could induce artificial errors in intensity ratio-based approaches. In addition, the inclusion of the nonlinear background may actually be beneficial under some conditions for the multivariate calibration model (e.g., for rich equivalence ratios as observed in Fig. 8 (b)). On the other hand, an obvious concern with both approaches is signal trapping, which can lead to significant errors in chemiluminescence-based equivalence ratio measurements. For example, sooty flames and other optically dense scenarios in practical combustors may impede the collection of chemiluminescence emissions, thus confounding or even completely preventing the sensing of equivalence ratios. To resolve these issues, a correction factor could be added to overcome the error introduced by signal trapping. However, in other practical combustors that encounter lean premixed flames or flameless (volumetric) combustion under low soot conditions (e.g., HCCI and lean-burn spark ignition engines), the proposed methodology may still be applied. Another difficult situation could arise in high-pressure combustion environments, as spectral peak intensities in chemiluminescence spectra are pressure-dependent [4]. Therefore, it is important to ensure that the calibration process for both the multivariate calibration model as well as the OH^*/CH^* intensity ratio calibration model is performed under practically relevant pressure conditions.

A potential benefit of the multivariate calibration methodology may be realized when sensing equivalence ratios in recirculation zones in combustors where exhaust gas may mix with the fresh fuel-air mixture or in IC engines with significant residual or recycled exhaust gas within the cylinder. Under these conditions, it may be necessary to revisit the definition of the parameter that quantifies mixture strength. The issue of redefinition of the equivalence ratio will also arise for oxygenated fuels (with oxygen atoms present in the fuel molecule), or when fuel molecules are present in the oxidizer [23]. Instead of using the traditional “fuel-air equivalence ratio,” it may be more meaningful to define and use an oxygen-based equivalence ratio to quantify mixture strength. Nevertheless, the authors believe that the chemiluminescence-based sensing methodology could still work under these conditions. The only difference would be that instead of using the traditional equivalence ratio to “calibrate” the multivariate calibration model, the variations in the spectral data associated with variations in the new quantity that characterizes mixture strength (e.g., oxygen-based equivalence ratio or fuel-oxygen ratio) should be used. In this manner, any other quantity (similar to equivalence ratio) can be predicted (after careful initial calibrations) using the multivariate data analysis methodology presented in this paper. Finally, the output from chemiluminescence-based sensors will also vary with variations in operating conditions of practical combustors. This must be considered carefully during the calibration process and the calibration data set must include as wide a range of practically relevant operating conditions as possible.

6. Conclusions

Real time measurement of local fuel-air equivalence ratios (φ) can be helpful in monitoring pollutant formation in premixed combustors, prevention of damages to combustors, and in the development of advanced combustion strategies, amongst other applications. In the present paper, a new partial least square regression (PLS-R) based multivariate sensing methodology was investigated and compared with an OH^*/CH^* intensity ratio-based calibration model for sensing equivalence ratio in atmospheric methane-air premixed flames, ranging from fuel-lean to fuel-rich conditions. Five replications of spectral data at nine different equivalence ratios ranging from 0.73 to 1.48 were used in the calibration of both models. An unbiased spectral data set (not used in the PLS-R model development), for 28 different equivalence ratio conditions ranging from 0.71 to 1.67, was used to predict equivalence ratios using the PLS-R and the intensity ratio calibration models. The major experimental results presented in this paper can be summarized as follows:

- Since the PLS-R model used raw spectral intensities from the entire spectrum, it did not need subtraction of the nonlinear background CO_2^* emission, which was required in the OH^*/CH^* intensity ratio calibration model to obtain OH^* and CH^*spectral peak intensities.
- The PLS-R based multivariate calibration model ensured a better calibration of the original spectral data set compared to the OH^*/CH^* intensity ratio calibration model with an improved R^2 value (0.97 to 0.99) value and lower root mean square error in calibration (0.05 to 0.02).

- The OH^*/CH^* intensity ratio calibration model grossly underpredicted equivalence ratios in the unknown spectral data set compared to measured equivalence ratios, especially under rich conditions ($\varphi > 1.2$). By comparison, the PLS-R based multivariate calibration model performed better in predicting equivalence ratios (to within 7 percent of measurements) from the unknown spectral data set

These results demonstrate a proof-of-concept for the development of multivariate sensing strategies for monitoring and/or control of equivalence ratios in practical combustors. Further studies are required to evaluate the performance of the multivariate calibration model in high-pressure environments and for premixed flames with other fuels. Finally, the multivariate measurement methodology needs to be demonstrated and validated in practical premixed combustors.

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