DEMONSTRATION OF TEMPERATURE AND OH MOLE FRACTION DIAGNOSTIC IN $\text{SiH}_4/\text{H}_2/\text{O}_2/\text{Ar}$ FLAMES USING NARROW-LINE UV OH ABSORPTION SPECTROSCOPY

M. T. DONOVAN, D. L. HALL, P. V. TOREK, C. R. SCHROCK AND M. S. WOOLDRIDGE

*Department of Mechanical Engineering
University of Michigan
2350 Hayward St.
Ann Arbor, MI 48109-2125, USA*

Results of an experimental study of the application of frequency-modulated UV laser absorption spectroscopy to silica (SiO_2) particle-forming flames ($\text{SiH}_4/\text{H}_2/\text{O}_2/\text{Ar}$) are presented. An argon-ion pumped ring-dye laser system in the rapid wavelength scanning configuration was used to obtain multiple line shape profiles of the $\text{R}_1(7)$ and $\text{R}_1(11)$ transitions in the $\text{A}^2\Sigma^+ \leftarrow \text{X}^2\Pi_i$ (0,0) band of the OH spectrum ($\nu_o = 32,625.547$ and $32,625.072 \text{ cm}^{-1}$, respectively). Temperature and OH mole fraction were determined by a best fit of a convolved Voigt absorption profile to the data. Measurements were made in the multiphase regions of silane/hydrogen/oxygen/argon flames, verifying the applicability of the diagnostic approach to combustion synthesis systems. Absorption measurements were taken over a range of particle environments found at increasing heights above the burner surface (5–20 mm) and equivalence ratios ($\phi = 1.0$ and 1.2). The experimental data were compared with thermocouple measurements, equilibrium, and one-dimensional modeling simulations. The results of the study successfully demonstrate OH UV absorption spectroscopy as a highly sensitive and accurate (uncertainties less than $\pm 10\%$ in the current work) diagnostic approach for *in situ* measurements of temperature and OH mole fractions in combustion synthesis flames.

Introduction

Gas-phase combustion synthesis (GPCS) of nanostructured materials is a powerful synthesis method, capable of generating high-purity materials [1,2] with controlled particle size, size distribution, morphology, and composition [3,4]. However, the fundamental mechanisms governing the formation of nanosized materials are not well understood, particularly the process of particle nucleation [1,2]. Experimental methods and diagnostic tools, which can be used to improve our knowledge of the physical and chemical processes important in GPCS, are vital to developing combustion synthesis technologies and realizing the potential of nanostructured materials. In particular, knowledge of the temperature field is critical because temperature and residence time are two of the most important factors affecting particle formation and growth [1,2]. In addition, quantitative data on key intermediate species (such as OH and SiO) will help develop and validate models and aid in understanding the role of chemical kinetics in combustion synthesis systems.

Numerous researchers have made quantitative measurements of temperature and/or species concentration in particle-containing flames. Hanson [5] and Roth and Brandt [6,7] have demonstrated the ability to use rapid wavelength scanning absorption spectroscopy in the IR to measure gas concentra-

tions (CO and CO_2) in carbonaceous particle-forming flames. Torek et al. [8] used a scanning semiconductor diode laser in the IR to measure temperature and water concentrations in $\text{SiH}_4/\text{H}_2/\text{O}_2/\text{Ar}$ flames with high silica particle loadings. Zachariah and co-workers [9–11] have used laser-induced fluorescence (LIF) to make OH concentration measurements in ceramic particle-forming counterflow diffusion flames. Hwang et al. [12] used nitrogen coherent anti-stokes Raman spectroscopy (CARS) to make temperature measurements and planar LIF to make qualitative OH concentration measurements, both in particle-containing flames. The absorption technique demonstrated in this paper offers an alternative, sensitive method to make simultaneous *in situ*, line-of-sight measurements of temperature and species mole fraction in particle-containing flames using UV modulation absorption spectroscopy. Advantages of using the narrow-line rapid wavelength scanning approach include good spatial resolution, rapid time response, and absolute quantitative measurements with low uncertainties, as demonstrated by Rea and Hanson [13]. An additional important characteristic is that the approach can be used in systems with high particle loadings. Also, unlike LIF-based techniques, data analysis and interpretation does not depend on quenching rates, which may have considerable uncertainties. This work presents the first application of UV narrow-line absorption spectroscopy to a

FIG. 1. Schematic of the OH absorption diagnostic including top view of the multi-element diffusion burner.

nanoparticle combustion synthesis system. Demonstration of the concept has considerable implications, as the UV spectral region contains resonance transitions of a number of key intermediate species in addition to OH, which are important in silicon synthesis systems (e.g., SiO, Si, and SiH [14,15]). Therefore, the objective of this study was to demonstrate that the rapid UV laser wavelength scanning absorption approach could be used for accurate and precise measurements of T and χ_{OH} in a benchmark silane/hydrogen/oxygen ($\text{SiH}_4/\text{H}_2/\text{O}_2$) flame system.

Experimental

Experiments were conducted using a Hencken multi-element diffusion burner (Research Technologies, RD1X1) at atmospheric pressures. The Hencken burner was selected for the ability to produce nominally one-dimensional flat flames with essentially homogeneous conditions orthogonal to the direction of flow. Thermocouple measurements show that the temperature profile is essentially uniform (less than 5% variation from the mean temperature) in the horizontal plane parallel to the surface of the burner at heights greater than 5 mm. Similarly, Hancock et al. [16] used nitrogen and hy-

drogen CARS to make temperature measurements which confirmed the one-dimensional nature of a slightly larger Hencken burner.

Details of the combustion synthesis facility are given in Torek [17] and Torek et al. [8]. Briefly, the burner is a 25.4 mm square array of hypodermic fuel tubes and oxidizer channels (Fig. 1). Each fuel tube is sealed from the oxidizer channels, and fuel/oxidizer mixing occurs at the exit plane of the burner. A 6.4 mm wide inert gas coflow is used to isolate the flame from the surrounding air and to improve flame stability. Reactant flow rates were measured using a mass flow meter (O_2 : TSI, model 4100, $\pm 2\%$ accuracy) and calibrated rotameters (H_2 , Ar, SiH_4 : Omega, $\pm 5\%$ accuracy).

The OH absorption diagnostic is depicted in Fig. 1. The laser source was an intracavity frequency-doubled ring dye laser (Coherent 899-05, Rhodamine 6G dye, KDP doubling crystal) pumped by an argon-ion laser (514 nm, ~ 6.2 W, Coherent Innova 420). The ring-dye laser was tuned to scan the $R_1(7)$ and $R_1(11)$ transitions in the $A^2\Sigma^+ \leftarrow X^2\Pi_1(0,0)$ band of the OH spectrum ($\nu_0 = 32,625.547$ and $32,625.072$ cm^{-1} for the two transitions, respectively). Frequency scanning was accomplished using a galvanometer-driven Brewster plate in the laser cavity. The scan width was 2.0 cm^{-1} (~ 60 GHz), and scans were completed in approximately 0.8 s (1.25 Hz).

TABLE 1
Spectroscopic parameters used in determination of OH line strengths and OH line broadening half-widths

Transition	J'	J''	ν_o (cm ⁻¹)	E'' (cm ⁻¹)	A_{ul} (s ⁻¹)	$2\gamma_{o,A}$ (cm ⁻¹ atm ⁻¹)		n_A	
						Ar	H ₂ O	Ar	H ₂ O
R ₁ (7)	8.5	7.5	32,625.547	1026.754	261,600	0.0325	0.11	-0.8	-0.35
R ₁ (11)	12.5	11.5	32,625.072	2413.614	274,800	0.0325	0.094	-0.8	-0.19

The wavelength of the visible output of the ring dye laser was measured at the start of a scan using a wavemeter (Advantest TQ8325). A scanning interferometer (Fabry-Perot étalon, 2 GHz free spectral range, Burleigh SA Plus Laser Spectrum Analyzer) was used to monitor the laser mode quality and the relative laser frequency during the scan.

The UV beam (~0.5 mm diameter) passed through the gases above the surface of the burner orthogonal to the direction of the flow. Amplified photodiode detectors (3 dB response times <12.3 μs, Perkin-Elmer HUV-1100BQ) were used to monitor the reference and absorbed laser emission intensities. A 1.5 GHz digital oscilloscope (Hewlett Packard, Infinium 54845) was used to record the incident (I_o), transmitted (I), and differenced ($I_o - I$) laser intensities and the étalon signal. A typical data set consisted of three sweeps in the "forward" direction (increasing wavenumber) and two sweeps in the "reverse" direction.

Spectroscopic Model

The attenuation of incident radiation by a homogeneous absorbing medium is described using the Beer-Lambert relation:

$$-\ln \frac{I(v)}{I_o} = S_{lu} \phi(v) p \chi_{OH} L \quad (1)$$

where I_o is the intensity of the incident radiation, p is the total pressure (atm), χ_{OH} is the mole fraction of OH, L is the path length through the absorbing medium (cm), ν is the frequency of the radiation (cm⁻¹), and S_{lu} is the integrated line strength (cm⁻² atm⁻¹) of the transition from the lower state (l) to the upper state (u). The line shape function $\phi(v)$ is based on a normalized Voigt function [18,19].

The determination of the collisional-broadening half-width is particularly important, as this parameter is highly dependent on the composition of the mixture being interrogated. Given the large mole fractions of argon and water in the experiments conducted for this study, all broadening is assumed to occur only by argon and water. The methodology of Rea et al. [19] is used to calculate the collisional

broadening half-width. Broadening properties for argon and water (the pressure-independent collision broadening parameter, $2\gamma_o$ [cm⁻¹ atm⁻¹], and the temperature exponent, n) were obtained from Rea et al. [19] and Rea [20].

Goldman and Gillis [21] provide the following expression used to determine S_{lu} :

$$S_{lu} = \frac{1}{8\pi c \nu_o^2} \frac{N_{OH}}{p} \frac{e^{-hcE''/kT}}{Q_{int}} A_{ul} (2J' + 1) \times (1 - e^{-hc\nu_o/kT}) \quad (2)$$

Here, Q_{int} is the total molecular partition function, A_{ul} is the Einstein A-coefficient for spontaneous emission (sec⁻¹), E'' is the lower state energy (cm⁻¹), ν_o is the resonant transition frequency (cm⁻¹), and N_{OH} is the number density of OH molecules (molecules/cm³). The transition parameters used in equation 2 were obtained from Gillis et al. [22,23]. All spectroscopic model input parameters are summarized in Table 1. Q_{int} was calculated by direct summation using the rotational term values from Stark et al. [24] and spectroscopic constants from Luque and Crosley [25].

Based on the above expressions and given prescribed values of p , L , and the broadening parameters $2\gamma_o$ and n , it can be seen that equation 1 is a function of only temperature and χ_{OH} . Given a profile of $I(v)/I_o$ over a frequency range covering the absorption features of interest (e.g., the R₁(7) and R₁(11) transitions), equation 1 can be solved iteratively to determine the temperature and χ_{OH} that provide the best fit between the data and model. This procedure is described in detail below.

If equation 1 is evaluated at the apparent peaks of the R₁(7) and R₁(11) absorption lines, and the ratio of the two expressions is taken, the ratio of the peak transmissivities is only a function of S_{lu} and $\phi(v)$. Therefore, for a given gas composition (i.e., fixed broadening parameters) and pressure, the peak height ratio of the two absorption lines is only a function of the gas temperature. The temperature dependence of the intensity ratio has been demonstrated by previous researchers [26, and references therein] to significantly increase the sensitivity of temperature measurements made using frequency-modulated laser absorption spectroscopy.

FIG. 2. Typical unprocessed absorption data for the $R_1(7)$ and $R_1(11)$ transitions of the $\text{OH } A^2\Sigma^+ \leftarrow X^2\Pi_i(0,0)$ spectrum (non-particle-forming flame, $\phi = 1.0$, $z = 7$ mm, $L = 2.54$ cm).

FIG. 3. Analyzed OH absorption data corresponding to the unprocessed data of Fig. 2. Best-fit model results are shown as the dashed line: $T = 1505$ K, $\chi_{\text{OH}} = 997$ ppm. Dotted and dot-dashed lines represent best-fit profiles for temperatures ± 100 K of $T = 1505$ K.

Data Analysis

Figure 2 shows a portion of a typical unprocessed data trace obtained during a scan of the $R_1(7)$ and $R_1(11)$ transitions in a non-particle-forming $\text{H}_2/\text{O}_2/\text{Ar}$ flame. All data are presented in the frequency domain relative to the peak of the $R_1(7)$ transition, where the data have been converted from the time domain to the frequency domain using the spacing of the étalon fringes (Fig. 2). In the frequency domain, a linear offset is applied to the reference signal to correct for any zero offset deviations caused by beam drift during the scan and/or signal loss due to particle scattering or absorption in the particle-producing flames. This correction can be applied to the signal beam, as opposed to the reference beam; the

FIG. 4. Analyzed OH absorption data corresponding to a particle-forming flame ($\phi = 1.2$, $z = 6$ mm). Best-fit model results are shown as the dashed line: $T = 1614$ K, $\chi_{\text{OH}} = 1004$ ppm. Dotted and dot-dashed lines represent best-fit profiles for temperatures ± 100 K of $T = 1614$ K.

effect on the absorption signal is the same in either case. After this adjustment has been performed, the transmittance ratio, $I(v)/I_0$, is calculated. The DC shift due to particle scattering and/or absorption was measured in a spectral region free of any OH absorption features and found to be approximately 0.7% and independent of wavelength. Failure to account for this small DC shift can lead to an inability to recover the wings of the absorption profile.

At this point, an initial temperature and χ_{OH} are selected and the $S_{ij}\phi(v)p\chi_{\text{OH}}L$ product is determined using equation 2. The temperature and χ_{OH} are then varied in order to minimize the residual (defined as the sum-of-the-square differences between the experimental data and the model results). The same analysis approach was used for both non-particle-forming and particle-forming flames.

Results and Discussion

The results of the data analysis procedure are presented in Fig. 3 ($\text{H}_2/\text{O}_2/\text{Ar}$ flame) and Fig. 4 ($\text{SiH}_4/\text{H}_2/\text{O}_2/\text{Ar}$ flame). Comparison of Figs. 3 and 4 shows there are no fundamental differences in the absorption traces between the gas-phase and the multiphase flames. Note the high quality of fit, where the maximum normalized residual (defined as the difference between the data and the best-fit profiles, normalized by the maximum absorption) is less than $\pm 5\%$ for the entire range of the scan. Figs. 3 and 4 also include profiles assuming temperatures ± 100 K relative to the best-fit temperature. Note the clear deviations from the experimental data for these profiles, particularly at the resonance transition frequencies. The quality of the fit is apparent

TABLE 2
Experimental conditions^a

Case	ϕ^b	Flow Rate (L min ⁻¹)				
		H ₂	SiH ₄	O ₂	Ar	N ₂
1	1.0	2.93	0	1.466	17.99	28.32
2	1.2	3.52	0	1.466	17.99	28.32
3	1.0	2.71	0.055	1.466	18.23	28.32
4	1.2	3.25	0.066	1.466	18.28	28.32

^aAll experiments were conducted at atmospheric pressure.^bThe determination of the equivalence ratio includes consideration of both H₂ and SiH₄ as fuel species.

FIG. 5. Temperature as a function of height above the burner, H₂/O₂/Ar flame, $\phi = 1.0$. Each spectroscopic data point represents the average of three measurements. Spectroscopic temperature data: $\blacktriangle$; spectroscopic OH mole fraction data, $\blacksquare$; thermocouple data, $\bullet$. T_{ad} = adiabatic flame temperature.

by comparing the residuals of the data (e.g., Fig. 3: the sum of the squares of the residuals for the best fit is 0.15; for the +100 K case, it is 0.24, and for the -100 K case, it is 0.25). The large deviations indicate the high sensitivity of the two-line absorption technique for temperature determination.

In order to demonstrate the technique over a range of combustion synthesis conditions, data were obtained in H₂/O₂/Ar and SiH₄/H₂/O₂/Ar flames at heights ranging from 5 to 20 mm above the burner surfaces. Given the one-dimensional nature of the burner system, increasing distance above the surface of the burner corresponds to increasing particle residence time and different heights correspond to different particle number densities, sizes, and morphology (typically, discrete particles are present at

lower heights and branchy agglomerates and aggregates exist at higher elevations). Measurements were made below 5 mm, but interpretation of these data was complicated by inhomogeneties in the flow close to the burner surface. Measurements at locations higher than 20 mm exhibited low signal-to-noise ratios due to rapidly decreasing absorption (due to decreased χ_{OH}). In addition to varying the height at which measurements were made, equivalence ratios of $\phi = 1.0$ and 1.2 were studied. Fuel-rich conditions were chosen for examination due to the more adverse experimental conditions presented by higher particle loadings (particle concentration estimated at $>1 \times 10^{11}$ particles/cm³, assuming complete conversion of silane to silica and an average particle diameter of $d_p \approx 20$ nm). A summary of the conditions studied is presented in Table 2.

The temperatures and χ_{OH} values determined for the experimental conditions are summarized in Figs. 5–8. As noted above, each measurement at a given height consisted of multiple forward and reverse sweeps of the frequency-modulated UV laser beam. Independent analysis of each sweep was conducted, and the resulting best-fit temperatures and OH mole fractions were averaged. (The average standard deviations were $\sim 1\%$ for both temperature and χ_{OH} . The maximum standard deviations in temperature and χ_{OH} were 2.3% and 3.7%, respectively.) For comparison, in the two particle-free flames (Figs. 5 and 6), radiation-corrected fine-wire thermocouple measurements are also shown. Except at lower elevations, where catalytic effects are assumed to be significant, agreement between the thermocouple data and the temperatures determined via the OH absorption diagnostic is quite good.

In previous work using a similar Hencken burner, Hancock et al. [16] demonstrated the near adiabatic nature of the Hencken burner. While the flow rates used in their study were considerably higher than those used here (and thus would enhance the adiabatic nature of the burner), it was expected that the burner conditions used in this study would result in near adiabatic conditions. To investigate this assumption, the STANJAN chemical equilibrium

FIG. 6. Temperature as a function of height above the burner, $\text{H}_2/\text{O}_2/\text{Ar}$ flame, $\phi = 1.2$. Each spectroscopic data point represents the average of three measurements. Spectroscopic temperature data, $\blacktriangle$; spectroscopic OH mole fraction data, $\blacksquare$; thermocouple data, $\bullet$. T_{af} = adiabatic flame temperature.

solver [27] was used to evaluate the adiabatic flame temperature (T_{af}) and the equilibrium species concentrations for the four flame conditions studied. For the calculations, the reactants were assumed to be at 298 K and 1 atm. The adiabatic flame temperatures were determined assuming constant pressure and enthalpy and are shown in Figs. 5–8. The dashed horizontal lines indicate the uncertainties in T_{af} due to uncertainties in the reactant flow rate measurements. As seen in Figs. 5–8, the calculated profile is bounded by the adiabatic flame temperature (within the uncertainty of the calculations) for each condition investigated. While not shown in Figs. 5–8, the calculated equilibrium χ_{OH} is lower than the OH mole fraction measured using the laser diagnostic by a factor of 0.4–2 orders of magnitude. The results indicate the gases have not yet reached chemical equilibrium by 20 mm above the burner surface.

Due to the relatively low concentrations of silane in the particle-producing flames, the temperature profiles were not expected to substantially deviate from those of the $\text{H}_2/\text{O}_2/\text{Ar}$ flames. This is observed in the temperature profiles of Figs. 5–8. Regarding the OH profiles, oxidation of silane to SiO_2 will occur preferentially to the oxidation of the hydrogen at fuel-rich conditions. Therefore, for $\phi > 1.0$ flames, the silane systems will have fewer sources for OH (such as O atoms and H_2O) and hence lower concentrations of OH. Comparing the OH mole fractions in Figs. 6 and 8, it can be seen that at higher

FIG. 7. Temperature as a function of height above the burner, $\text{SiH}_4/\text{H}_2/\text{O}_2/\text{Ar}$ flame, $\phi = 1.0$. Each spectroscopic data point represents the average of three measurements. Spectroscopic temperature data, $\blacktriangle$; spectroscopic OH mole fraction data, $\blacksquare$. T_{af} = adiabatic flame temperature.

elevations (15 and 20 mm above the burner surface), there is indeed a lower concentration of OH in the flames containing silane compared to the pure $\text{H}_2/\text{O}_2/\text{Ar}$ flames.

To investigate the possibility of non-equilibrium conditions, the PREMIX/CHEMKIN 3 library [28] was used to model the reaction environment. While the one-dimensional homogeneous model used by PREMIX does not accurately describe the mixing conditions in the first few millimeters above the burner surface, the results of a PREMIX analysis may be used to infer trends downstream of the initial mixing zone. The chemical mechanism used with the PREMIX modeling can be found in Ref. [29]. Results of the PREMIX analysis and the assumed temperature profiles for the $\text{H}_2/\text{O}_2/\text{Ar}$ flames are shown in Figs. 5 and 6. Note that while the temperature profiles below 5 mm are somewhat arbitrary, changing the temperature profiles only shifts the χ_{OH} profile downstream of 5 mm; it does not fundamentally change the shape of the χ_{OH} profile. As can be seen in the figures, the PREMIX results accurately capture the decrease in χ_{OH} at higher elevations above the burner surface and clearly show that non-equilibrium conditions still persist at 20 mm above the burner surface. Significantly improved quantitative agreement between the PREMIX results and the data was achieved by adjusting the rate coefficients of two of the reactions within their reported uncertainty limits. However, given the limitations of PREMIX to represent the non-uniform conditions

FIG. 8. Temperature as a function of height above the burner, $\text{SiH}_4/\text{H}_2/\text{O}_2/\text{Ar}$ flame, $\phi = 1.2$. Each spectroscopic data point represents the average of three measurements. Spectroscopic temperature data, ▲; spectroscopic OH mole fraction data, ■. T_{af} = adiabatic flame temperature.

near the burner surface, the adjustment of rate coefficients to achieve a better cosmetic fit with the spectroscopic data was not considered meaningful, and results of the modified mechanism are not included in this report. PREMIX analyses of the $\text{SiH}_4/\text{H}_2/\text{O}_2/\text{Ar}$ flames were attempted using the silane combustion mechanism published by Babushok et al. [30]. Due to the complexity of the silane combustion mechanism, the PREMIX solver was unable to converge to a reasonable solution for the silane flames. However, the OH concentration is clearly not in chemical equilibrium for the combustion synthesis flames, either.

An uncertainty analysis was undertaken to quantify the accuracy of the temperature and χ_{OH} measurements made using the laser absorption diagnostic. Uncertainties in the spectroscopic parameters result in a corresponding uncertainty in the calculated temperature and χ_{OH} of $\pm 2.1\%$ and $\pm 1.1\%$, respectively. Uncertainty in the absorption path length directly translates into uncertainty in the χ_{OH} . Based on horizontal thermocouple measurements made at various heights above the burner surface, the variation in absorption path length is estimated at $\pm 8\%$ (2 mm). Due to the rapid recombination of OH at lower temperatures, any uncertainty due to diffusion of OH into the cold shroud gas flow is considered to be small and is incorporated in the uncertainty due to path length. The application of DC offsets, as described in the analysis section, results in an estimated maximum uncertainty of 4% in tem-

perature and 5% in χ_{OH} . Due to the change in product mole fractions, uncertainties in the flow rates contribute an uncertainty of 0.2% in temperature and 0.1% in χ_{OH} . Combining the sources of uncertainty yields an overall uncertainty of 4.6% in temperature and 9.5% in χ_{OH} .

Based on a noise level of $\sim 1\%$ of the reference signal strength, $P = 1$ atm, $T = 1500$ K, broadening parameters typical of the mixtures studied and a path length of 2.54 cm, the sensitivity of the diagnostic presented herein is estimated at 25 ppm. Based on the low level of scattering ($< 0.7\%$) caused by nanoparticles at the loadings studied in this work, it is anticipated that the current diagnostic could be used in flames with much higher particle loadings.

Summary and Conclusions

Frequency-modulated laser absorption spectroscopy has been demonstrated as an accurate, sensitive, and robust method for *in situ* temperature (uncertainty of $\sim \pm 5\%$) and OH mole fraction (uncertainty of $\sim \pm 10\%$) determinations in SiO_2 particle-forming flames. In particular, absolute and quantitative measurements of temperature and χ_{OH} over the range of particle environments found at increasing heights above the burner surface (5–20 mm) and varying equivalence ratios ($\phi = 1.0$ and 1.2) have been obtained in the multiphase regions of silane/hydrogen/oxygen flames. The results are in good agreement with thermocouple measurements, equilibrium, and one-dimensional modeling simulations. The results indicate that the combustion gases are not in chemical equilibrium below 20 mm above the surface of the burner for both particle- and non-particle-forming flames.

The OH UV rapid wavelength scanning absorption diagnostic shows considerable promise for extensive use in gas-phase combustion synthesis studies. The ability to obtain high-quality temperature and species measurements in the adverse conditions encountered in combustion synthesis environments, without the need for extensive empirical calibrations, makes it an invaluable research tool.

Acknowledgments

The generous support of the National Science Foundation (Dr. Farley Fisher, program monitor), the Sloan Foundation, and the Michigan Space Grant Consortium is gratefully acknowledged.

REFERENCES

1. Pratsinis, S. E., *Prog. Energy Combust. Sci.* 24:197 (1998).
2. Wooldridge, M. S., *Prog. Energy Combust. Sci.* 24:63 (1998).

3. Wegner, K., and Pratsinis, S. E., *KONA, Powder Part.* 19:170 (2000).
4. Zachariah, M. R., and Semerjian, H. G., *High Temp. Sci.* 28:113 (1990).
5. Hanson, R. K., *Appl. Opt.* 19:482 (1980).
6. Roth, P., and Brandt, O., *AIP-Conf. Proc.* 208:506 (1990).
7. Brandt, O., and Roth, P., *Combust. Flame* 77:69 (1989).
8. Torek, P. V., Hall, D. L., Miller, T. A., and Wooldridge, M. S., *Appl. Opt.* 41:2274 (2002).
9. Zachariah, M. R., and Burgess Jr., D. R. F., *J. Aerosol Sci.* 25:487 (1994).
10. Zachariah, M. R. and Semerjian, H. G., *AIChE J.* 35:2003 (1989).
11. Zachariah, M. R., *Laser Diagnostic Measurements During Aerosol Processing of Ceramic Powders, Ceramic Powder Science III* (G. Messing, ed.), American Ceramic Society, Westerville, OH, 1989, pp. 283–290.
12. Hwang, J. Y., Gil, Y. S., Kim, J. I., Choi, M., and Chung, S. H., *J. Aerosol Sci.* 32:601 (2001).
13. Rea Jr., E. C., and Hanson, R. K., *Appl. Opt.* 27:4454 (1988).
14. Kampas, K. J., and Griffith, R. W., *Sol. Cells* 2:385 (1980).
15. Shanker, R., Linton, C., and Verma, R. D., *J. Mol. Spectrosc.* 60:197 (1976).
16. Hancock, R. D., Bertagnolli, K. E., and Lucht, R. P., *Combust. Flame* 109:323 (1997).
17. Torek, P. V., “H₂O Absorption Spectroscopy for the Study of Gas-Phase Combustion Synthesis Using a Multi-Element Burner,” M.S. thesis, Mechanical Engineering Department, University of Michigan, Ann Arbor, 2001.
18. Bernath, P. F., *Spectra of Atoms and Molecules*, Oxford University Press, New York, 1995, p. 29.
19. Rea Jr., E. C., Chang, A. Y., and Hanson, R. K., *J. Quant. Spectrosc. Radiat. Transfer* 37:117 (1987).
20. Rea Jr., E. C., “Rapid-Tuning Laser Wavelength Modulation Spectroscopy with Applications in Combustion Diagnostics and OH Line Shape Studies,” Ph.D. thesis, Mechanical Engineering Department, Stanford University, Stanford, CA, 1991.
21. Goldman, A., and Gillis, J. R., *J. Quant. Spectrosc. Radiat. Transfer* 25:111 (1981).
22. Gillis, J. R., Goldman, A., Stark, G., and Rinsland, C. P., *J. Quant. Spectrosc. Radiat. Transfer* 68:225 (2001).
23. Rothman, L. S., Rinsland, C. P., Goldman, A., Massie, S. T., Edwards, D. P., Flaud, J.-M., Perrin, A., Camy-Peyret, C., Dana, V., Mandin, J.-Y., Schroeder, J., McCann, A., Gamache, R. R., Wattson, R. B., Yoshino, K., Chance, K. V., Jucks, K. W., Brown, L. R., Nemtchinov, V., and Varanasi, P., *The HITRAN Molecular Spectroscopic Database and HAWKS (HITRAN Atmospheric Workstation): 1996 Edition*; *J. Quant. Spectrosc. Radiat. Transfer* 60:665 (1998); www.hitran.com.
24. Stark, G., Brault, J. W., and Abrams, M. C., *J. Opt. Soc. Am.* B11:3 (1994).
25. Luque, J., and Crosley, D. R., *J. Chem. Phys.* 109:439 (1998).
26. Chang, A. Y., DiRosa, M. D., Davidson, D. F., and Hanson, R. K., *Appl. Opt.* 30:3011 (1991).
27. W. C. Reynolds, *STANJAN Chemical Equilibrium Solver, Ver. 3.89*, Stanford University, Stanford, CA.
28. Kee, R. J., Rupley, F. M., Miller, J. A., Coltrin, M. E., Grcar, J. F., Meeks, E., Moffat, H. K., Lutz, A. E., Dixon-Lewis, G., Smooke, M. D., Warnatz, J., Evans, G. H., Larson, R. S., Mitchell, R. E., Petzold, L. R., Reynolds, W. C., Caracotsios, M., Steward, W. E., Glarborg, P., Wang, C., and Adigun, O., *CHEMKIN Collection, Release 3.6*, Reaction Design, San Diego, CA, 2000.
29. University of Michigan, Ann Arbor, 2002, www.personal.engin.umich.edu/~mswool/website/Research/.
30. Babushok, V. I., Tsang, W., Burgess Jr., D. R., and Zachariah, M. R., *Proc. Combust. Inst.* 27:2431 (1998).

COMMENTS

Wolfgang G. Bessler, *Heidelberg University, Germany.* Given the pronounced streak structure visible in the particle-laden flame, it seems that there are large spatial inhomogeneities in mole fractions and for temperatures. How does this affect the line-of-sight absorption measurement?

Author's Reply. Temperature measurements made orthogonal to the flow using fine wire thermocouples confirm the uniformity in the conditions in the *x-y* plane above the burner. Due to the rapid diffusion rates at the operating conditions of the burner, gas concentrations are expected to be similarly uniform. Due to their greater mass, particles will diffuse at much slower rates and will tend to follow streamlines. As the absorption measurements were made

across multiple streaks, the line-of-sight measurements encompassed a significant number density of particles. Although the number density is likely non-uniform, the absorption technique is relatively insensitive to particle loadings (as discussed in the text), and any variations in the particle density are not expected to affect the measurements.

•

A. S. Tezaki, *University of Tokyo, Japan.* The frequency modulation technique is a very nice way to obtain precise spectroscopic data with high sensitivity. On the other hand, it likely will be greatly influenced by residual or diffused

OH at the peripheral low T region even if the purge was quite perfect. How do you handle that?

Author's Reply. The decrease in temperature at the outer regions of the burner is extreme (on the order of 200 K/mm). Due to the large temperature gradients, any

OH that diffuses from the active region of the burner is expected to rapidly recombine. This effect was examined in the context of the uncertainty analysis and contributes to the uncertainty in the path length through the absorbing gases leading, to an effect on χ_{OH} of less than $\pm 8\%$ as noted in the text.