H$_2$O absorption spectroscopy for determination of temperature and H$_2$O mole fraction in high-temperature particle synthesis systems

Paul V. Torek, David L. Hall, Tiffany A. Miller, and Margaret S. Wooldridge

Water absorption spectroscopy has been successfully demonstrated as a sensitive and accurate means for in situ determination of temperature and H$_2$O mole fraction in silica (SiO$_2$) particle-forming flames. Frequency modulation of near-infrared emission from a semiconductor diode laser was used to obtain multiple line-shape profiles of H$_2$O rovibrational ($v_1 + v_2$) transitions in the 7170–7185-cm$^{-1}$ region. Temperature was determined by the relative peak height ratios, and $x_{H_2O}$ was determined by use of the line-shape profiles. Measurements were made in the multiphase regions of silane/hydrogen/oxygen/argon flames to verify the applicability of the diagnostic approach to combustion synthesis systems with high particle loadings. A range of equivalence ratios was studied ($\phi = 0.47–2.15$). The results were compared with flames where no silane was present and with adiabatic equilibrium calculations. The spectroscopic results for temperature were in good agreement with thermocouple measurements, and the qualitative trends as a function of the equivalence ratio were in good agreement with the equilibrium predictions. The determinations for water mole fraction were in good agreement with theoretical predictions but were sensitive to the spectroscopic model parameters used to describe collisional broadening. Water absorption spectroscopy has substantial potential as a valuable and practical technology for both research and production combustion synthesis facilities. © 2002 Optical Society of America

1. Introduction

Gas-phase combustion synthesis of particles is an industrially significant synthesis method for the production of numerous powder materials, including silica, titania, and carbon black. Because of the highly catalytic nature of the flow in combustion synthesis systems, conventional intrusive diagnostic methods (such as thermocouple measurements and gas sampling) are not reliable, and their presence can significantly alter the local conditions. Nonintrusive yet in situ diagnostics that can be used to interrogate the state conditions in these chemically reacting, particle-laden flow systems are highly desirable. Such diagnostic capabilities are critical to increase the understanding of the fundamental physical mechanisms important in combustion synthesis systems and to develop process and product relationships.

Absorption spectroscopy by use of semiconductor diode lasers as the emission source has been well established as a means to determine temperature, pressure, velocity, and concentration of several important combustion species (e.g., CH$_4$, H$_2$O, and O$_2$) in traditional hydrocarbon combustion systems. Semiconductor diode lasers are particularly well suited for application to production facilities in that they are generally durable, small, and inexpensive. In addition, the data can be analyzed rapidly leading to a viable and practical detection system for the basis of process control. Optical fibers and multiplexing also facilitate implementation of semiconductor laser absorption spectroscopy.

Hanson and Roth and co-workers have demonstrated the application of absorption spectroscopy to particle-laden flow using infrared diode lasers (cryogenically cooled lead-salt diode lasers). In the research by Hanson, the CO transition at 2137.20 cm$^{-1}$ was used to determine the CO partial pressure in highly sooting premixed acetylene/air flames generated with a commercial slot burner. Carbona-
cessous soot loadings were estimated to be $\sim 1 \times 10^9$–$1 \times 10^{10}$ particles/cm$^3$ based on laser extinction measurements. In the studies by Roth and co-workers,$^{13,14}$ CO and CO$_2$ transitions in the infrared (CO at 2176.2839 cm$^{-1}$ and CO$_2$ at 2369.0857 cm$^{-1}$) were used to determine soot oxidation rates in high-temperature flows containing dispersed soot particles (particle densities of $\sim 1 \times 10^8$–$1 \times 10^9$ particles/cm$^3$, with an average particle size of $\sim 100$ nm). Scattering and extinction of the laser emission by soot particles are typically small in the infrared spectral region. Thus interference from the particles was negligible for the conditions studied.

In the current study, the general approaches of the two absorption diagnostic methods described above are combined to form the basis of a new method to interrogate gas-phase combustion synthesis systems. Here, wavelength modulation of near-infrared emission from a semiconductor diode laser ($\lambda \sim 1.393$ $\mu$m) is demonstrated as a viable means for both thermometry and water-vapor concentration measurements in silica- (SiO$_2$) producing flames. Unlike carbonaceous soot, silica is not generally absorptive, having only a real portion of the refractive index.$^{15}$ Only scattering of the laser emission by particles is of concern. However, wavelength modulation of the laser emission allows complete resolution of several H$_2$O transition line shapes. Consequently, it is not necessary to explicitly model scattering from the SiO$_2$ particles. Any scattering effects are assumed constant throughout the small wavelength regions scanned ($\Delta \nu = \nu - \nu_0 \equiv 1.2$ cm$^{-1}$, for each spectral window), and any offset in the absorption spectra observed that is due to scattering can be accounted for in the data analysis. Because of the limited sensitivity to the presence of the particles, absorption spectroscopy has the potential to be a powerful tool for combustion synthesis studies.

Absorption spectroscopy based on H$_2$O rovibra-tional transitions was chosen as the basis for the diagnostic approach. Water is a particularly attractive species for the diagnostic development for several reasons. H$_2$O is a naturally occurring by-product of many combustion synthesis systems. Water vapor can occur in relatively high concentrations, and H$_2$O has strong absorption features in wavelength regions readily accessible by semiconductor diode lasers. In the following sections, the development and application of the diagnostic method are presented. Descriptions of the spectroscopic model and the combustion synthesis facility used and discussion of the results in the context of particle synthesis systems are also provided.

2. Spectroscopic Model

The diagnostic is based on line-of-sight absorption of laser emission, where both temperature and mole fraction of water vapor can be inferred from the transmissivity of the product gases in accordance with the Beer–Lambert relation:

$$
\tau(\nu) = I(\nu)/I_0 = 1 - \Delta I/I_0 = \exp[-S(T)\phi(\nu, T)P_{\text{H}_2\text{O}}L].
$$

Here $\tau(\nu)$ is the transmissivity at frequency $\nu$ (cm$^{-1}$), $I_0$ is the incident intensity of the laser emission, $I(\nu)$ is the intensity at frequency $\nu$ of the transmitted beam, $\Delta I = I_0 - I(\nu)$, $S(T)$ is the line strength of the transition (cm$^{-2}$ atm$^{-1}$), $\phi(\nu, T)$ is the line-shape function (cm), $P$ is the total absolute pressure (atm), $n_{\text{H}_2\text{O}}$ is the mole fraction of water vapor in the absorbing medium, and $L$ is the path length through the absorbing medium (cm). The line-shape function is modeled as a Voigt profile:

$$
\phi(\nu, T) = (2/\Delta \nu_{\text{Doppler}})\ln 2/\pi)^{1/2}V(a, w),
$$

where $w$ is the normalized frequency in the absence of collision shift,

$$
w = 2\ln(2)\nu/\nu_0/\Delta \nu_{\text{Doppler}},
$$

and the Voigt $a$ parameter is given by

$$
a = \ln 2/\Delta \nu_{\text{collision}}/\Delta \nu_{\text{Doppler}}.
$$

Each $\Delta \nu$ in Eqs. (2)–(4) is a half-width at half maximum (cm$^{-1}$). The Doppler half-width is a well-known function of temperature $T$ (K), molecular weight $M$ (amu), and transition frequency $\nu_0$ (cm$^{-1}$):

$$
\Delta \nu_{\text{Doppler}} = 3.581 \times 10^7 \nu_0^{1/2}/T/M,
$$

whereas the collisional half-width can be expressed as

$$
\Delta \nu_{\text{collision}} = \sum_i \Delta \nu_{i,\text{ref}} P_i (T/T_{\text{ref}})^{-n_i/2}.
$$

In Eq. (6) $\Delta \nu_{i,\text{ref}}$ is the half-width for collisional broadening of water by species $i$ at the reference conditions. For simplicity, because argon and water vapor account for the bulk of the product gases in this study, all gases other than water vapor were treated as argon. Nominal values for $\Delta \nu_{\text{H}_2\text{O},\text{ref}}$ (where $T_{\text{ref}} = 296$ K) were taken from the HITRAN database.$^{16}$ Nominal values for the temperature exponents for self-broadening were taken as the average value for $n_{\text{H}_2\text{O}-\text{H}_2\text{O}}$ as reported by Gamache et al.$^{17}$ For $\Delta \nu_{\text{Ar,ref}}$, the value for the air-broadening collisional half-width of each transition was taken from HITRAN.$^{16}$ We then modeled argon broadening at $T_{\text{ref}}$ by multiplying the HITRAN air-broadening parameters by 0.45, i.e.,

$$
\Delta \nu_{\text{Ar,ref}} = 0.45 \Delta \nu_{\text{air,ref}}.
$$

The 0.45 factor is a representative value for the ratio of the argon-broadened half-width to the nitrogen-broadened half-width for transitions near 7117 cm$^{-1}$, as determined by Nagali et al.$^{18}$ Nominal values for the temperature dependences of the argon-broadened half-width were assumed equal to the corresponding values for $n_{\text{H}_2\text{O}-\text{air}}$ taken from the HITRAN database.$^{16}$ Uncertainties in the collisional-broadening
parameters have limited effect on the temperature determinations. However, the collisional-broadening parameters have a significant effect on the determination of the mole fraction of water vapor. In the course of the study, it was found that modifications to the collisional-broadening factors ($\Delta v_{H_2O, ref}$, $n_{H_2O-H_2O}$, $\Delta v_{Ar, ref}$, and $n_{H_2O-Ar}$) yielded improved fits to the experimental data and improved agreement with theoretical predictions. The modifications were all within the uncertainty limits suggested by Gamache et al.\textsuperscript{17} in their survey of experimental results for the collisional-broadening parameters for H$_2$O. Table 1 presents both the nominal values for the collisional-broadening parameters and the actual values used in the model. The procedure to determine the improved values for the collisional-broadening parameters is discussed further in Section 5.

For a particular rovibrational transition, the line strength at temperature $T$ is given by

$$S(T) = \frac{S(T_{red})(T_{red}/T)[Q(T_{red})/Q(T)]\exp[-(hcE'/k)]}{(1/T - 1/T_{red})[1 - \exp(-hc\nu_0/kT)]/[1 - \exp(-hc\nu_3/kT)]},$$

(8)

where $h$ is Planck’s constant, $k$ is Boltzmann’s constant, $c$ is the speed of light in a vacuum (cm/s), $\nu_0$ is the resonant frequency of the transition (cm$^{-1}$), $E'$ is the energy of the lower state of the transition (cm$^{-1}$), and $Q(T)$ is the rovibrational partition function. The rigid-rotor, harmonic oscillator model for water was used to model the partition function, such that

$$Q(T) = \frac{0.5\pi ABC(kT/hc)^{1/2}}{1 - \exp(-hc\nu_1/kT)}[1 - \exp(-hc\nu_2/kT)][1 - \exp(-hc\nu_3/kT)],$$

(9)

where $A$, $B$, and $C$ are the three rotational constants of an asymmetric top rotor (27.0, 14.4, and 9.4 cm$^{-1}$, respectively, for water).\textsuperscript{20} The fundamental frequencies of vibration for water are $\nu_1 = 3657.05$ cm$^{-1}$, $\nu_2 = 1594.75$ cm$^{-1}$, and $\nu_3 = 3755.93$ cm$^{-1}$.\textsuperscript{21} For the relatively low temperatures studied in the current research ($T < 2000$ K), the rigid-rotor, harmonic oscillator model is within <3% of the values for the partition function obtained by a direct summation of the energy levels\textsuperscript{22} and agrees within 1.6% with the partition function expression provided in the HITRAN 92 database.\textsuperscript{23} Note that the effect of nuclear spin degeneracy ($g_{n,H_2O} = 4$) was omitted from Eq. (9) for simplicity. Because only ratios of the partition function are used in the spectroscopic model [see Eq. (8)], the omission does not affect the model results.

### Table 1. Data Used in the Spectroscopic Model for Major and Minor H$_2$O Absorption Features (Major Features Are in Bold Type)

<table>
<thead>
<tr>
<th>$v_0$ (cm$^{-1}$)</th>
<th>$\lambda$ ($\mu$m)</th>
<th>Transition$^a$</th>
<th>$J_{K,a,K,c}^n$</th>
<th>$J_{K,a,K,c}^s$</th>
<th>$S(T_{red})$ (cm/molecule) (uncertainty)</th>
<th>$E'$ (cm$^{-1}$)</th>
<th>$\Delta v_{Ar,ref}$ (cm$^{-1}$)</th>
<th>$n_{H_2O-Ar}$ (cm$^{-1}$)</th>
<th>$n_{H_2O,H_2O}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7173.779$^b$</td>
<td>1.3940</td>
<td>$v_1 + v_2$</td>
<td>$s_{0,3}$</td>
<td>$s_{0,2}$</td>
<td>$8.35 \times 10^{-23}$</td>
<td>1411.612</td>
<td>0.0368</td>
<td>0.62</td>
<td>0.3542</td>
</tr>
<tr>
<td>7179.752$^b$</td>
<td>1.3928</td>
<td>$v_1 + v_3$</td>
<td>$s_{1,1}$</td>
<td>$s_{0,2}$</td>
<td>$2.27 \times 10^{-22}$</td>
<td>1216.194</td>
<td>0.0268</td>
<td>0.63</td>
<td>0.3321</td>
</tr>
<tr>
<td>7181.114$^b$</td>
<td>1.3925</td>
<td>$v_1 + v_3$</td>
<td>$s_{0,3}$</td>
<td>$s_{0,2}$</td>
<td>$1.43 \times 10^{-20}$</td>
<td>1367.632</td>
<td>0.0451</td>
<td>0.75</td>
<td>0.4549</td>
</tr>
<tr>
<td>7182.950$^b$</td>
<td>1.3922</td>
<td>$v_1 + v_3$</td>
<td>$s_{1,0}$</td>
<td>$s_{1,2}$</td>
<td>$3.72 \times 10^{-21}$</td>
<td>142.279</td>
<td>0.0375</td>
<td>0.87</td>
<td>0.4148</td>
</tr>
<tr>
<td>7183.016$^b$</td>
<td>1.3922</td>
<td>$v_1 + v_3$</td>
<td>$s_{2,1}$</td>
<td>$s_{2,0}$</td>
<td>$4.60 \times 10^{-22}$</td>
<td>134.902</td>
<td>0.0451</td>
<td>0.68</td>
<td>0.8463</td>
</tr>
<tr>
<td>7183.273$^b$</td>
<td>1.3921</td>
<td>$v_1 + v_3$</td>
<td>$s_{0,5}$</td>
<td>$s_{0,5}$</td>
<td>$7.66 \times 10^{-24}$</td>
<td>1718.719</td>
<td>0.0290</td>
<td>0.65</td>
<td>0.2946</td>
</tr>
</tbody>
</table>

$^a$Data taken from HITRAN database.\textsuperscript{16}

$^b$Data taken from Toth.\textsuperscript{19}

$^c$Collisional-broadening data for H$_2$O broadened by air taken from HITRAN database\textsuperscript{16} modified within the error limits stated by Gamache et al.\textsuperscript{17} Actual values used in the data analysis are listed. Nominal values are listed in parentheses. See text for details.

$^d$The temperature dependence to collisional broadening of H$_2$O by argon was assumed equivalent to that for broadening by air. The values for $n_{H_2O-air}$ were taken from the HITRAN database\textsuperscript{16} modified within the error limits stated by Gamache et al.\textsuperscript{17} Actual values used in the data analysis are listed. Nominal values are listed in parentheses.

$^e$Collisional-broadening data for H$_2$O broadened by H$_2$O taken from HITRAN database\textsuperscript{16} modified within the error limits stated by Gamache et al.\textsuperscript{17} Actual values used in the data analysis are listed. Nominal values are listed in parentheses.

$^f$The temperature dependence to collisional broadening of H$_2$O by Ar is taken from Gamache et al.\textsuperscript{17} and modified within the error limits stated by the authors. Actual values used in the data analysis are listed. Average values of data from Gamache et al.\textsuperscript{17} are listed in parentheses.
The spectroscopic parameters for the five major absorption features examined in the study and several relevant minor features are given in Table 1. The transitions used in the study were selected on the basis of careful consideration of many important criteria including the sensitivity of the transition for $T$ and $\chi_{H_2O}$ determination, detectivity limits, isolation of the spectral feature, relative population of the associated energy levels at low and high temperatures, uncertainties in the associated spectral constants, and accessibility through existing semiconductor diode laser technology. The criteria were considered for the range of conditions found in typical combustion synthesis systems. Unfortunately, no single transition met the ideal standards of a well-known, strong, spectrally well-isolated, sensitive transition involving states populated only at high temperatures. The transitions used in the study represent a compromise that yields a sensitive and accurate diagnostic approach by use of multiple transitions, each with some of the favorable aspects outlined above. Calculated absorption spectra (specifically, the product $[S(T)\phi P_{\chi_{H_2O}}]$) at 1 atm, 15% H$_2$O (mole basis), and several temperatures are shown in Fig. 1. To account for possible contributions from overlapping lines, the entire spectrum from 7170 to 7185 cm$^{-1}$ as reported in HITRAN was modeled. The five major absorption features used in the current study are located at 7173.779, 7179.752, 7181.156, 7182.950, and 7183.273 cm$^{-1}$ and are noted in Fig. 1. Figure 2 shows the variation of the peak absorption of the primary spectral features as a function of temperature, normalized by the peak absorption of the $v_1 + v_3$ ($7_{0,1}$) transition, i.e., $R_i = [S(v = v_0)\text{Transition } i/ S_{7(0,1)}\phi(v_0 = 7179.752 \text{ cm}^{-1})]$. The 7170–7185-cm$^{-1}$ (1.3918–1.3947-μm) spectral region was selected for study in particular because of the strong line strengths at the conditions of interest, and the features in this region show good sensitivity to temperature as indicated in Figs. 1 and 2, respectively.

3. Experimental Details
To evaluate the hypothesis that absorption spectroscopy by use of semiconductor diode lasers can be used in combustion synthesis applications, we conducted experiments using a laboratory-scale combustion synthesis burner facility. The burner is a multielement diffusion burner (MEDB) or Hencken burner. The MEDB consists of a 2.54-cm-square array of small nonpremixed fuel tubes and oxidizer channels surrounded by a 0.64-cm-wide shroud region, as shown in Fig. 3. The burner is also equipped with a central fuel tube with an independent gas manifold to...
The experimental arrangement used for the majority of the absorption spectroscopy experiments is shown in Fig. 4. An InGaAsP diode laser (Sensors Unlimited, SU-1393-DFB) was used to provide near-infrared emission in the 7173–7184 cm\(^{-1}\) (1.392–1.394-\(\mu\)m) range. The emission wavelength was controlled by temperature and current tuning. A triangular current function with a ramp period of ~100 ms was used to modulate the emission across the absorption line-shape features. Table 3 lists the reactants used and the corresponding purities. All experiments were conducted at ~1 atm.

The experimental arrangement used for the major- as shown in Fig. 4, a portion of the laser emission was sampled by use of a beam splitter and recorded before it passed over the burner. The main transmitted portion of the emission was multipassed in a horizontal plane above the surface of the burner, through the postflame gases (total path length in postflame gases is approximately equal to 7.63 cm). A portion of the transmitted emission was directed onto a confocal etalon (Burleigh SA-92-B1, free spectral range of 2 GHz) to monitor the relative spectral location of the modulated emission. Emission intensities were monitored with amplified germanium detectors (Judson J16-5SP-R02M-HS), and the angles of the beam splitters were adjusted until the two detectors received equal emission intensities when no flame was present. The incident \(I_0\) and transmitted \(I\) emission signals were recorded with a digital oscilloscope sampling at 2.5 kHz (Agilent Infinium, 54845A, 1.5 GHz). The etalon signal and the difference between the detector signals \(\Delta I\) obtained with a differential probe (Agilent, 1153A, 200 MHz), were also recorded.

### 4. Data Analysis

As noted above, several transition features were used to develop the temperature and water mole fraction diagnostic. Use of multiple transitions reduced the experimental uncertainty in the measurements and the sensitivity of the temperature determination to the \(\chi_{\text{H}_2\text{O}}\) determination. Similar to the technique developed by Arroyo and Hanson\(^6\) and Chang et al.\(^25\) ratios of the absorption peak heights relative to the peak height of the \(v_1 + v_3\) \((76,1)\) transition (7179.752 cm\(^{-1}\)) were used to determine temperature, i.e.,

\[
R(T, \chi_{\text{H}_2\text{O}}) = \left[ \frac{\ln[I(v_0)/I_0]}{\ln[I(v_0)/I_0]} \right]_{(76,1)} = \left[ \frac{[S(T)\phi(v_0, T)]_{(76,1)}}{[S(T)\phi(v_0, T)]_{(76,1)}} \right]. \quad (10)
\]

As can be seen in Fig. 2, this approach yields good sensitivity to temperature for conditions found in combustion synthesis systems. Note that, unlike some earlier studies,\(^6,25\) ratios of the spectrally integrated absorption coefficients were not used, and consequently the ratios \(R_i\) are a function of both \(T\) and \(\chi_{\text{H}_2\text{O}}\). However, the ratios are weak functions of \(\chi_{\text{H}_2\text{O}}\) with each ratio varying by less than 3% over the range of water mole fractions encountered in the ex-

### Table 2. Reactant Purities

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Purity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH₄</td>
<td>99.99</td>
</tr>
<tr>
<td>H₂</td>
<td>99.99</td>
</tr>
<tr>
<td>Ar*</td>
<td>99.998</td>
</tr>
<tr>
<td>O₂*</td>
<td>99.993</td>
</tr>
<tr>
<td>N₂ (shroud gas)</td>
<td>99.998</td>
</tr>
</tbody>
</table>

*O₂ and Ar were premixed by Cryogenic Gases: 7.4% O₂, balance argon (mole basis).

### Table 3. Laser Operating Conditions

<table>
<thead>
<tr>
<th>Wavelength Region Scanned (cm(^{-1}))</th>
<th>Case Temperature (°C)</th>
<th>Current Modulation Frequency (Hz)</th>
<th>Average Injection Current (mA)</th>
<th>Baseline Injection Current (ramp start) (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7173.2–7174.6</td>
<td>20.0</td>
<td>10</td>
<td>61.5</td>
<td>48</td>
</tr>
<tr>
<td>7179.2–7180.4</td>
<td>6.6</td>
<td>10</td>
<td>57.0</td>
<td>39</td>
</tr>
<tr>
<td>7180.7–7181.9</td>
<td>3.2</td>
<td>10</td>
<td>55.0</td>
<td>38</td>
</tr>
<tr>
<td>7182.5–7183.7</td>
<td>–0.7</td>
<td>10</td>
<td>53.0</td>
<td>36</td>
</tr>
</tbody>
</table>
periments. Use of Eq. (10), as opposed to ratios of the integrated absorption coefficients, simplifies both data collection and data analysis, which is particularly desirable for sensor control applications. Once the temperature was determined by a least-squares fit to the four peak-height ratios (with an approximate value for $\chi_{\text{H}_2\text{O}}$ based on complete combustion assumptions), the best fit to all five line-shape profiles was used to determine the mole fraction of water vapor present.

Data analysis was also used to correct for absorption by ambient H$_2$O vapor present in the beam path, beam-steering effects, and entrainment of flame-produced H$_2$O in the shroud gas. To account for potential absorption by moist air in the room, baseline $\Delta I$ data were recorded before and after each set of experiments with dry gases flowing through the burner. The average of the baselines was subtracted from the $\Delta I$ data before analysis. The effects of baseline corrections typically resulted in changes of less than 5% in the absorption peak heights.

Beam-steering effects that are due to density gradients were also addressed in the data analysis. The absorption measured in the far wings of each wavelength region, where absorption should be near zero for several of the features (see Fig. 1), was assumed to be the theoretical value for the nonresonant absorption at a temperature of 1000 K and a water-vapor mole fraction corresponding to thermodynamic equilibrium conditions. The line shape was vertically translated such that the absorption in the far wings normalized to the absorption at $v_0$ matched the theoretical normalized value. Note that the effects that are due to beam steering were small for most experiments, and the corrections changed the absorption peak heights by less than 5% and usually considerably less than this amount.

Entrainment (and the resulting cooling) of the flame-produced water by the shroud gases was also accounted for in the data analysis. Because the $v_1 + v_0$ ($3_{0,3}$) and the $v_1 + v_0$ ($3_{1,3}$) lines are much stronger at lower temperatures (see Fig. 1), even a small amount of cold water vapor can contribute significantly to the measured strength of these lines. It was therefore necessary to account for absorption by H$_2$O at the edge of the flame separately from absorption by H$_2$O at the center of the flame. Consequently, in the absorption model, the absorbing region above the burner was divided into three zones based on data obtained from experiments at the edge of the flame. We delineated the three zones by differing values of $\chi_{\text{H}_2\text{O}}$ and $T$ and included an outer edge zone 2 mm wide, an inner zone of the same width, and a hot water-rich core zone (see Fig. 5). The excess temperature (gas temperature minus shroud gas temperature, $\Delta T$) and the mole fraction of water vapor hypothesized in the core zone were treated as step functions as shown in Fig. 5. The values of $T$ and $\chi_{\text{H}_2\text{O}}$ as proportions of the corresponding values in the core, were determined from single-pass edge experiments ($H_2/O_2/Ar, \phi = 0.93$). Absorption observed in the outer zones was subtracted from that in the inner zones before we analyzed the inner-zone data. Temperature and mole fraction of water vapor both remain constant within less than 2 mm of the edge of the active burner area and then decrease sharply with horizontal distance. An additional (inner) 2-mm-wide edge zone was examined in the current study, but the temperature and water vapor observed in that zone were not significantly different from the corresponding values in the core region. The $\Delta T$ baseline and beam-steering corrections described above were also used to interpret the data from the edge experiments. Here, beam steering was severe and the correction could lead to as much as a 20% difference in peak height. If the cold H$_2$O were not accounted for by use of the three-zone model, the inferred temperature would be ~15% lower, which would increase the absorption coefficients of all the transitions, except the $v_0 = 7173.779$ cm$^{-1}$ and $v_0 = 7183.273$ cm$^{-1}$ transitions, which remain approximately constant. As a result of the higher absorption coefficients, the inferred mole fraction of water vapor would be lower by ~30%. Thus, without the three-zone model, both the temperature and the mole fraction of water vapor would be underestimated.

5. Results and Discussion

Near-infrared H$_2$O absorption spectroscopy was used to measure the temperature and water vapor in the product gases of both particle-forming (SiH$_4$/H$_2$/O$_2$/Ar) and non-particle-forming (H$_2$/O$_2$/Ar) flames. Table 4 lists the range of reactant conditions studied. Equivalence ratios ($\phi$) listed are the quotients of the actual fuel:air ratios divided by the stoichiometric fuel:air ratio. Stoichiometric conditions are assumed to lead to complete conversion of all silicon to SiO$_2$ and all hydrogen to H$_2$O. Each experiment with silane is a single perturbation of a comparable experiment with a H$_2$/O$_2$/Ar flame. In each case, a
The mixture of 18.5% silane in argon was added in fixed proportion to the hydrogen flow rate. The proportion was kept low to minimize silica accumulation at the exit of the fuel tubes. (Silica particles formed in the flame are thermophoretically driven toward the cool burner surface.) Assuming complete conversion of the silane to silica particles and using a representative particle diameter of \( d_p = 20 \text{ nm} \) (based on transmission electron microscopy of the particles), we estimated silica particle loadings of \( \sim 4 \times 10^{11} \text{ particles/cm}^3 \).

Representative absorption data obtained at a height \( z = 30 \text{ mm} \) above the surface of the burner are shown in Figs. 6 and 7. Figure 6 presents results for a non-particle-forming flame, and Fig. 7 presents the complementary results for a particle-forming flame. The corresponding flow conditions for the experiments are given in Table 4, \( \phi = 0.43 \) and \( \phi = 0.47 \). Figures 6 and 7 both show the four wavelength regions considered. The experimental data shown are the average of approximately five scans per wavelength region. Each scan takes \( \sim 0.1 \text{ s} \) to acquire, with a total acquisition time of \( \sim 10 \text{ min} \) for all wavelength regions. Although the burner is nominally steady, peak heights varied from scan to scan by \( \sim 2–4\% \) of the mean values. We converted the time basis of the data to frequency using the known separation between the peaks in the etalon signal, with linear interpolation used between each pair of peaks. Note that the spacing between the \( v_1 + v_3 (3,0,3) \) and \( v_1 + v_3 (10,5,8) \) transitions is consistent with the results of the study by Toth \(^{19} \) of near-infrared \( \text{H}_2\text{O} \) spectra. The line spacing is larger than that reported in the HITRAN database \(^{16} \) by \( \sim 0.063 \text{ cm}^{-1} \). Also shown in Figs. 6 and 7 are the best-fit results of the theoretical model and the resulting optimized values for \( T \) and \( \chi_{\text{H}_2\text{O}} \). The residuals [the difference between the experimental data and the modeling results normalized by the peak height of the \( v_1 + v_3 (3,0,3) \) transition] are also presented in Figs. 6 and 7 and show the high-quality fit that can be obtained for both particle-forming and non-particle-forming flames (residuals typically less than 10% throughout the wavelength region examined).

During the study, it was found that the determinations for the mole fraction of water vapor were systematically lower than the theoretical predictions by \( \sim 50\% \). The transition strengths are relatively well known with low uncertainties (see Table 1). However, the collisional-broadening parameters for the specific transitions have larger uncertainties [Gamache and co-authors state that a two-standard-deviation (2\( \sigma \)) uncertainty in the broadening param-

### Table 4. Reactant Conditions (in Liters per Minute)

<table>
<thead>
<tr>
<th>( \phi )</th>
<th>( \text{SiH}_4 )</th>
<th>( \text{H}_2 )</th>
<th>( \text{O}_2 )</th>
<th>( \text{Ar} )</th>
<th>( \text{N}_2 ) shroud</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.42</td>
<td>0.000</td>
<td>1.12</td>
<td>1.32</td>
<td>16.4</td>
<td>28.3</td>
</tr>
<tr>
<td>0.47</td>
<td>0.029</td>
<td>1.13</td>
<td>1.32</td>
<td>16.6</td>
<td>28.3</td>
</tr>
<tr>
<td>0.69</td>
<td>0.000</td>
<td>1.81</td>
<td>1.32</td>
<td>16.4</td>
<td>28.3</td>
</tr>
<tr>
<td>0.75</td>
<td>0.039</td>
<td>1.82</td>
<td>1.32</td>
<td>16.6</td>
<td>28.3</td>
</tr>
<tr>
<td>0.93</td>
<td>0.000</td>
<td>2.45</td>
<td>1.32</td>
<td>16.4</td>
<td>28.3</td>
</tr>
<tr>
<td>1.01</td>
<td>0.049</td>
<td>2.47</td>
<td>1.32</td>
<td>16.7</td>
<td>28.3</td>
</tr>
<tr>
<td>1.39</td>
<td>0.000</td>
<td>3.68</td>
<td>1.32</td>
<td>16.4</td>
<td>28.3</td>
</tr>
<tr>
<td>1.51</td>
<td>0.068</td>
<td>3.71</td>
<td>1.32</td>
<td>16.7</td>
<td>28.3</td>
</tr>
<tr>
<td>2.00</td>
<td>0.000</td>
<td>5.29</td>
<td>1.32</td>
<td>16.4</td>
<td>28.3</td>
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<tr>
<td>2.16</td>
<td>0.097</td>
<td>5.31</td>
<td>1.32</td>
<td>16.9</td>
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<tr>
<td>0.80( ^a )</td>
<td>0.000</td>
<td>2.35</td>
<td>1.47</td>
<td>18.5</td>
<td>28.3</td>
</tr>
<tr>
<td>1.00( ^a )</td>
<td>0.000</td>
<td>2.93</td>
<td>1.47</td>
<td>18.5</td>
<td>28.3</td>
</tr>
<tr>
<td>1.50( ^a )</td>
<td>0.000</td>
<td>4.41</td>
<td>1.47</td>
<td>18.5</td>
<td>28.3</td>
</tr>
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</table>

\( ^a \)Conditions used to obtain the thermocouple data.
eters is 10–15% (Ref. 17)], which have significant effects on the inferred values for $\chi_{H_2O}$. Consequently, two representative data sets at $z = 15$ mm, $\phi = 0.6$ and $z = 15$ mm, $\phi = 2.0$ (for both particle-forming and non-particle-forming collisions) were used to modify the collisional-broadening parameters $(\Delta v_{H_2O, ref} n_{H_2O-H_2O}, \Delta v_{Ar, ref} n_{H_2O-Ar})$ within the respective uncertainty limits. All parameters for a particular transition were incrementally modified simultaneously to the same fraction of a 2σ deviation. For a given transition, all parameters were modified so as to broaden, or to narrow, the modeled line shape at temperatures greater than $T_{ref}$. The final set of collisional-broadening parameters was determined by a coarse estimate of the line widths required to minimize the residuals for the four representative spectra. With the exception of the transition at 7182.950 cm$^{-1}$ (modified by 15%), the average change in the nominal collisional-broadening data was less than 6.5%. The final values for $\Delta v_{H_2O, ref} n_{H_2O-H_2O}$, $\Delta v_{Ar, ref} n_{H_2O-Ar}$ (listed in Table 1) led to significantly improved fits to the spectral data (residuals typically less than 10%, as opposed to 20% before the collisional-broadening parameters were modified) and much improved agreement with the theoretical predictions (discussed further below). The changes in the broadening parameters led to slight changes in the temperature determinations (<18% throughout the range of conditions studied). The negative value for absorption present on the low-frequency side of the $v_1 + v_3$ ($3_{1,3}$) transition (see Figs. 6 and 7, $\lambda \equiv 7183$ cm$^{-1}$) is due to the beam-steering correction and indicates a limitation in the correction method. Ideally, the absorption in the wings of the line shape will approach zero for the transitions selected for study. However, if there is significant absorption in the wings, which is nonconstant as a function of wavelength (e.g., because of another nearby transition), the correction method should be modified to account for the interference. The correction method was not modified in this case because only one feature was affected, and use of multiple transitions reduces the sensitivity of the $T$ and $\chi_{H_2O}$ measurements to this concern.

Figure 8 summarizes the results determined for temperature as a function of the equivalence ratio for both the H$_2$-fueled flames and the SiH$_4$/H$_2$-fueled flames for a height of $z = 15$ mm. Adiabatic flame temperatures calculated with the chemical equilibrium program STANJAN$^{26}$ are also shown. For the equilibrium calculations, an initial temperature of 298 K and a pressure of 1 atm were assumed. Horizontal error bars in Fig. 8 reflect uncertainties in the flow measurements. Vertical error bars reflect primarily uncertainties in the transition strength and broadening data.

As can be seen in Fig. 8, the measured temperatures fall below the adiabatic flame temperatures by ~300–500 K throughout the range of conditions studied. However, the trend of temperature with equivalence ratio is in good qualitative agreement with the equilibrium calculations. The temperature differences between the H$_2$-fueled flames and the corresponding H$_2$/SiH$_4$-fueled flames are also in good agreement with those predicted by equilibrium calculations. The lower temperatures observed in the experimental data are likely due to nonuniformities in the probed flow conditions or approximations made in the absorption zone model described above. At typical, well-behaved operating conditions, the flow arrangement of the fuel tubes and oxidizer channels of the MEDB leads to a slightly dimpled flame surface. Close to the surface of the burner, i.e., $z < 5$–7 mm, temperature gradients in the $z$ direction determined by fine-wire thermocouples (type S, Pt-90%Pt/10%Rh, 25-μm bead diameter, Omega Engineering) were large, of the order of 200 K/mm. In general, mixing and diffusion rapidly smooth the gradients, resulting in nearly one-dimensional conditions at higher $z$ locations. Yet, fine-wire thermocouple measurements of the H$_2$/O$_2$/Ar flames indicated that the fuel lean conditions studied in the current research occasionally led to thermal nonuniformities of approximately 100 K in the horizontal plane parallel to the burner surface, i.e., nonplanar flame sheets. The temperature measurements made with the fine-wire thermocouples are shown in Figs. 8 and 10 and are within 12% of those determined by use of absorption spectroscopy. Note that the thermocouple data are uncorrected for radiation effects; however, radiation corrections are typically much less than 100 K for the small bead diameters used here and the experimental conditions studied. Also note, because the line-of-sight absorption measurements represent path-length-averaged values, the results for $T$ would necessarily be lower than adiabatic equilibrium predictions.

The experimentally determined values for the mole fraction of water vapor as a function of the equiva-
lence ratio at $z = 15$ mm are shown in Fig. 9. Calculated values for $\chi_{H_2O}$ based on adiabatic flame conditions are also included. The vertical error bars in Fig. 9 are primarily due to uncertainties in the temperature determination and the collisional-broadening data. Even though the collisional-broadening data were optimized for the $z = 15$ mm, $\phi = 0.6$, and $\phi = 2.0$ conditions, the measured values for $\chi_{H_2O}$ are in excellent agreement with the predicted equilibrium values throughout the entire range of equivalence ratios studied.

Measurements of $T$ and $\chi_{H_2O}$ were also taken at $z = 30$ mm (where particle loadings are potentially higher or particle restructuring has occurred, e.g., more agglomerated particles). An equivalent quality of fit to the absorption spectra was obtained for these data. Figures 10 and 11 summarize the results for $T$ and $\chi_{H_2O}$ as a function of equivalence ratio, $z = 15$ mm and $z = 30$ mm, for both particle-forming ($SiH_4 + H_2$) and non-particle-forming ($H_2$) flames. Vertical error bars denote the uncertainties in the spectroscopic data.

6. Conclusions

Line-of-sight water absorption spectroscopy ($\lambda = 1.39 \mu m$) has been successfully demonstrated as an accurate, sensitive, and robust method for in situ temperature (uncertainty of approximately $\pm 20\%$) and water mole fraction (uncertainty of approximately $\pm 35\%$) determination in SiO$_2$ particle-forming flames. In particular, absolute and quantitative measurements for $T$ and $\chi_{H_2O}$ have been obtained for $\phi = 0.47$–2.15 in the multiphase regions of silane/hydrogen/oxygen flames. The results are in good agreement with trends predicted by use of equilibrium calculations. The results of the current study also clearly motivate improved determinations of the collisional-broadening data for the water transitions in the 1.39-\mu m region.

Knowledge of the temperature field is critical in combustion synthesis systems to predict and control particle nucleation, growth, and restructuring mechanisms. Temperature measurements can also provide feedback on the status of the synthesis process and the resulting quality of the materials produced.
The successful application of absorption spectroscopy to nonintrusive, in situ measurements in combustion synthesis of powder materials therefore represents an exciting and significant breakthrough in diagnostic development for these systems.

Although path-averaged results have been presented, local determinations can be made with standard deconvolution techniques, such as Abel transformations. Thus the diagnostic technique can be readily applied to other common combustion synthesis burner geometries, such as coflow arrangements. The sensitivity of the diagnostic to H\textsubscript{2}O concentrations also facilitates application of the approach to systems with both high and low levels of water vapor present. If higher concentrations are expected, weaker transitions can be used and the multipassing arrangement eliminated. If lower concentrations are expected, additional multipassing can be used to increase signal-to-noise ratio levels. In addition, the time required to obtain the spectra can be reduced considerably by use of multiple diode lasers operating at different emission wavelengths, thus enabling a more rapid time response that may be necessary for the manufacture of control applications. Also, because water vapor is often present as a by-product of the combustion synthesis process, the diagnostic approach may not require the flow to be seeded with a probe species. Alternatively, other key species can be used such as CH\textsubscript{4} or O\textsubscript{2}. Last, the accuracy of the diagnostic technique can be further improved by validation of the high-temperature line strengths and collisional-broadening data.

Although near-infrared, diode laser absorption spectroscopy has been applied to chemical vapor deposition thin-film combustion synthesis systems, to the best of our knowledge, this study is the first demonstration of the application to combustion synthesis of ceramic particles. The diagnostic approach offers considerable advantages in comparison with alternative intrusive gas-sampling techniques. Given the versatility of semiconductor diode laser technology, in particular with respect to fiber-coupling technology, laser absorption spectroscopy holds considerable promise as a tool for process monitoring and control in particle synthesis applications.

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References


