

## High-sensitivity interference-free diagnostic for measurement of methane in shock tubes



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### ABSTRACT

A sensitive CW laser absorption diagnostic for *in-situ* measurement of methane mole fraction at high temperatures is developed. The selected transitions for the diagnostic are a cluster of lines near  $3148.8\text{ cm}^{-1}$  from the R-branch of the  $\nu_3$  band of the  $\text{CH}_4$  absorption spectrum. The selected transitions have 2–3 times more sensitivity to  $\text{CH}_4$  concentration than the P-branch in the  $3.3\text{ }\mu\text{m}$  region, lower interference from major interfering intermediate species in most hydrocarbon reactions, and applicability over a wide range of pressures and temperatures. Absorption cross-sections for a broad collection of hydrocarbons were simulated to evaluate interference absorption, and were generally found to be negligible near  $3148.8\text{ cm}^{-1}$ . However, minor interference from hot bands of  $\text{C}_2\text{H}_2$  and  $\text{C}_2\text{H}_4$  was observed and was characterized experimentally, revealing a weak dependence on wavelength. To eliminate such interferences, a two-color on-line and off-line measurement scheme is proposed to determine  $\text{CH}_4$  concentration. The colors selected, i.e., for on-line ( $3148.81\text{ cm}^{-1}$ ) and off-line ( $3148.66\text{ cm}^{-1}$ ), are characterized between 0.2–4 atm and 500 K–2100 K by absorption coefficient measurements in a shock tube. Minimum detectable levels of  $\text{CH}_4$  in shock tube experiments are reported for this range of temperatures and pressures. An example measurement is shown for sensitive detection of  $\text{CH}_4$  in a shock tube chemical kinetics experiment.

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### 1. Introduction

$\text{CH}_4$  is a stable and simple hydrocarbon that is commonly used as a fuel and can be produced as a major intermediate species during combustion of other hydrocarbons. Sensitive high-bandwidth measurements of  $\text{CH}_4$  mole fraction would provide important data in studies of reaction pathways and reaction rates in combustion kinetics. Numerous articles have been reported in the literature for designing  $\text{CH}_4$  sensors by utilizing the

strongest transitions in the  $\nu_3$  rovibrational band of the  $\text{CH}_4$  absorption spectrum [1–10]. However, most of these sensors were designed for room temperature applications. Pyun et al. [10] designed a DFG laser (generating light at  $2938.24\text{--}2938.01\text{ cm}^{-1}$ ) sensor for high-temperature (1000–2000 K)  $\text{CH}_4$  over a pressure range of 1.3–5.4 atm, for fast detection in a shock tube using a two-color peak-minus-valley absorption subtraction technique. The absorption transitions were in the P-branch of the  $\text{CH}_4$   $\nu_3$  band. This differential measurement strategy was based on the fact that most of the absorbance from interfering species varies weakly over such small wavelength ranges. By implementing their technique, interference-subtracted measurements were possible, but the amount of interference from other hydrocarbon species was significant,

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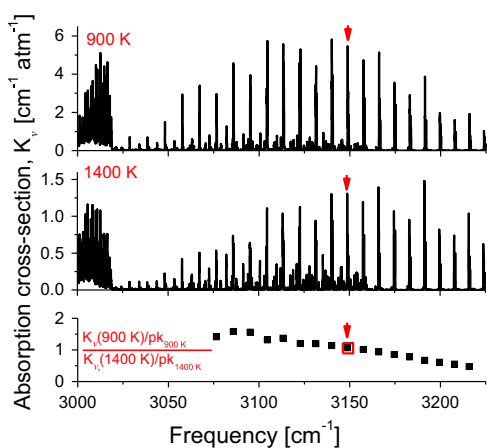
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leading to increased uncertainty and reduced sensitivity for the CH<sub>4</sub> mole fraction determination. Other previous work included the use of semiconductor diode lasers at 1.65 and 2.29 μm [11–22], mid-IR difference-frequency-generation (DFG) systems at 3.2–3.6 μm [1–9], interband cascade lasers (ICLs) at 3.3 μm [23,24], a liquid-He-cooled, lead-salt diode laser at 7.4 μm [25] and a quantum cascade laser at 8.1 μm [26,27]. Some of these studies [19–22] were designed for temperatures suitable for combustion exhaust applications (< 1200 K). However, none of these studies addressed the possibility of interference from the commonly encountered intermediate products of combustion at elevated temperatures (> 1200 K).

In this article, we present an improved sensor design based on transitions of CH<sub>4</sub> in the R-branch with significantly higher sensitivity and low interference from 35 common combustion intermediate species/radicals. The currently selected transitions completely avoid the strong absorption band due to the C–H stretch common to nearly all hydrocarbons near 3.3 μm. The current work also demonstrates the use of a recently developed DFB interband cascade laser (ICL) operating at 3.176 μm (Nanoplus [28]). Lastly, a sample high-bandwidth and high-SNR measurement of CH<sub>4</sub> is demonstrated during the pyrolysis of C<sub>3</sub>H<sub>8</sub> in a shock tube kinetics experiment.

### 1.1. Sensor design and selection of CH<sub>4</sub> transitions

A cluster of CH<sub>4</sub>  $\nu_3$   $^1A_1 \rightarrow ^1F_2$  R(14) A, F and E symmetry transitions near 3148.8 cm<sup>-1</sup> was selected for the sensor. The selected transitions show the best performance from the standpoints of interference and peak absorbance. Fig. 1 shows simulations based on the HITRAN 2012 [29] database for the R-branch of the  $\nu_3$  band of CH<sub>4</sub> at 900 K and 1400 K at 1 atm. Clearly, the selected region has a peak absorption coefficient among the top 4 of the entire band



**Fig. 1.** Absorption coefficient simulations of CH<sub>4</sub> based on HITRAN 2012 at 1 atm and 900 K and 1400 K. The red arrow indicates the selected cluster of transitions. The ratio of the peak absorption coefficients of the major lines at 900–1400 K normalized by the band maximum at respective temperatures are shown in the third plot. The selected line has a value close to 1 indicating optimal line selection. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

for both of these temperatures, which is the approximate temperature range of interest for the intended shock tube application of combustion chemistry studies. Also, shown in the same plot is the ratio of the peak absorption coefficients normalized by the band peak at 900 K to the same at 1400 K. The selected line has a value close to 1 showing optimal line selection over this temperature range.

Fig. 2(a) shows the absorption coefficients of common combustion intermediates (computed using HITRAN 2012 [29]) at 1400 K and 1 atm that absorb near this region. There are OH transitions that interfere with the CH<sub>4</sub> cluster at 3140 cm<sup>-1</sup> and there is some interference from the C<sub>2</sub>H<sub>2</sub> bands at the CH<sub>4</sub> clusters above 3157 cm<sup>-1</sup> (the hot bands important at these temperatures are undocumented in HITRAN'12 [29] database and hence not quantified). In addition, possible interference from 25 other combustion species was investigated using the Fourier transform infrared spectroscopy (FTIR) measurements by Klingbeil et al. [30,31]. Fig. 2(b) shows the most significant results at 773 K, which was used to select a region with minimum interference (absorption coefficient less than 5% that of CH<sub>4</sub> at 3148.81 cm<sup>-1</sup>). Out of the species studied, C<sub>2</sub>H<sub>4</sub> produced the highest interference (4% of the peak CH<sub>4</sub> absorption coefficient at 773 K, also discussed later) and some other species, shown in Fig. 2(c), indicate 1–3% (but spectrally unstructured) interference. The small ripples seen in the spectra of the higher hydrocarbons in Fig. 2(c) are artifacts of the FTIR instrument data analysis. In typical hydrocarbon pyrolysis experiments, the absorbance from the interfering species can be quite significant (~10%). However, with the two-color technique implemented in this work, this interference could be reduced to 0.5% error in measured CH<sub>4</sub> concentration. A list of studied interfering species with low interference at 3148.81 cm<sup>-1</sup> is given in Appendix A. Most previous work on high-temperature diagnostics of methane [10,32,33] used CH<sub>4</sub> transitions lower than 3000 cm<sup>-1</sup>. Clearly from Fig. 2(b), it can be seen that the interference from the higher hydrocarbons (e.g., ethane, *n*-pentane and *n*-heptane) dominate the P-branch of the  $\nu_3$  band. For a sensor designed to measure only CH<sub>4</sub> in a combustion product environment, the reduced interference near the selected absorption window provides a clear advantage over any line previously studied in the P-branch (including the work using HeNe lasers [32]). In addition, the R-branch peak absorption coefficient is about 2 times as strong as the peak of the P-branch. The initial line selection was done manually with the help of long range simulation programs written by the authors and the FTIR spectrum obtained experimentally in Adam Klingbeil's [30,31] work. This selection is optimal for the broad range of conditions mentioned (i.e., 900–1400 K, set of interfering species). If the range of temperatures and the set of interfering species are changed, the optimal selection would also change.

Although the interference near the selected transitions was minimal, it was found upon further investigation that there is a low but measurable amount of interference at 3148.81 cm<sup>-1</sup> from the hot bands of C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>, that are not recorded in HITRAN 2012 [29] or the FTIR surveys [30,31]. However, the spectra of C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>, measured

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