Quantitative Detection of Combustion Species using Ultra-Violet Diode Lasers

J. S. Pilgrim and K. A. Peterson
Southwest Sciences, Inc. 1570 Pacheco Street, Suite E-11 Santa Fe, NM 87505

INTRODUCTION

Southwest Sciences is developing a new microgravity combustion diagnostic based on UV diode lasers. The instrument will allow absolute concentration measurements of combustion species on a variety of microgravity combustion platforms including the Space Station. Our approach uses newly available room temperature UV diode lasers, thereby keeping the instrument compact, rugged and energy efficient. The feasibility of the technique was demonstrated by measurement of CH radicals in laboratory flames. Further progress in fabrication technology of UV diode lasers at shorter wavelengths and higher power will result in detection of transient species in the deeper UV. High sensitivity detection of combustion radicals is provided with wavelength modulation absorption spectroscopy.

It has long been recognized that absorption spectroscopy can provide quantitative species number densities, but the technique has not been used widely by combustion researchers because of poor sensitivity. In addition, one has to perform multiple line-of-sight measurements followed by tomographic inversion in order to retrieve spatial distribution information. We have been developing high frequency wavelength modulation spectroscopy (WMS) techniques utilizing commercially available visible, near-infrared, and mid-infrared diode lasers.[1-7] We have demonstrated minimum detectable absorbances of ~10^{-6} while retaining the inherent quantitative aspects of traditional absorption methods. This level of sensitivity— about a thousand times better than traditional absorption methods— allows detection of trace species including free radicals in flames.

In an earlier SBIR project sponsored by NASA Glenn Research Center, we successfully demonstrated high sensitivity detection of CH radicals in laboratory diffusion flames using ~100μW of tunable 426 nm generated by doubling 85 mW of 852 nm diode laser output in a nonlinear crystal. Results from the study are detailed in Optics Letters.[7] In another earlier SBIR project sponsored by NASA Lewis Research Center, we performed multiple line-of-sight measurements of H_2O and CH_4 under microgravity conditions to reconstruct 2-D distributions using the Abel inversion technique.[8] We have also extended the diode laser-based WMS technique to 308 nm by sum frequency mixing 488 nm Ar^+laser light and 835 nm diode laser light, and we demonstrated the high sensitivity detection of OH by WMS.[9]

Recently, GaN-based ultraviolet diode lasers became commercially available from Nichia Corporation in the 390 – 420 nm wavelength region. Operating at room temperature and emitting > 5 mW of continuous output, they were developed primarily for high density storage and printing applications. We recognize that new sensing applications may be available with ultraviolet diode lasers including combustion diagnostics and chemical analysis. In order to examine the spectroscopic properties and the feasibility of optical diagnostics based on UV diode lasers, we chose to monitor the CH radical in laboratory flames. The direct UV output from a GaN diode laser bypasses the requirement for a complex nonlinear upconversion step as performed in the earlier Phase I study.

Table I lists some of the combustion species that may be amenable to detection using the present diagnostic technique. The last two entries in the table, NO and O_2, require deep UV generation by first amplifying the UV diode laser output in a GaN power amplifier diode, followed by doubling in a nonlinear crystal. Such GaN power amplifier diodes have been demonstrated in the laboratory and are slowly becoming commercially available.

Table I. Combustion species amenable to UV diode lasers.

Species	Transition	Wavelength (nm)
CH	$A^2\Delta \leftarrow X^2\Pi$ $B^2\Sigma^- \leftarrow X^2\Pi$	413 – 440 387 – 408
C_2	$d\ ^3\Pi_g \leftarrow a\ ^3\Pi_u$ (Swan band)	438 – 516
CN	$B\ ^2\Sigma^+ \leftarrow X\ ^2\Sigma^+$	359 – 422
NO_2	$B\ ^2B_2 \leftarrow X\ ^2A_1$	350 – 780
NO	$A\ ^2\Sigma^+ \leftarrow X\ ^2\Pi_2$ (γ-band)	227, 215, 205 (x2)
O_2	$B\ ^3\Sigma_u^- \leftarrow X\ ^3\Sigma_g^-$ (Schumann-Runge)	175 – 205 (x2)

SPECTROSCOPIC APPLICATION OF GaN LASERS

One of the most serious impediments to applying GaN blue lasers to spectroscopic detection of combustion species is the erratic spectral coverage. Because only about 10 % of the wavelengths in the laser's nominal operating range are accessible for single mode tuning and modulation, there is no guarantee that an absorption feature of the target molecular species will be accessible. This limitation becomes even more disabling for molecules with sparse absorption features where there may be no absorption lines accessible to the GaN laser. Our solution is the development of a new type of external cavity diode laser (ECDL) that allows complete spectral coverage and agile wavelength tuning and modulation using GaN blue lasers.

The Southwest Sciences ECDL design allows the laser to be tuned by varying the diode gain element injection current. Thus, wavelength modulation frequencies may be orders-of-magnitude higher than with competitive presently commercialized designs (New Focus, Newport, and TuiOptics). Fig. 1 shows the wavelength tuning of our ECDL with diode laser injection current. Competitive designs approach wavelength modulation frequencies of about 1500 Hz limited by piezo-electric driven mechanical movement of an optical element. Our ECDL has been modulated at over 10 kHz and frequencies in the MHz regime are possible. The wavelength modulation frequency has important ramifications for implementation as a microgravity combustion diagnostic. First, the $1/f$ noise term dictates that higher frequency operation will result in increased sensitivity. Since we are interested in looking at weak molecular optical transitions of gaseous species that are present at low concentrations in a flame, the highest sensitivities are required. Secondly, the modulation frequency determines the temporal measurement resolution during the microgravity drop experiment; a higher frequency permits faster measurements. Thus, we can acquire data with higher temporal and spatial resolution during a 2.2 or 5.18 second drop than possible with slower commercial off-the-shelf ECDLs.

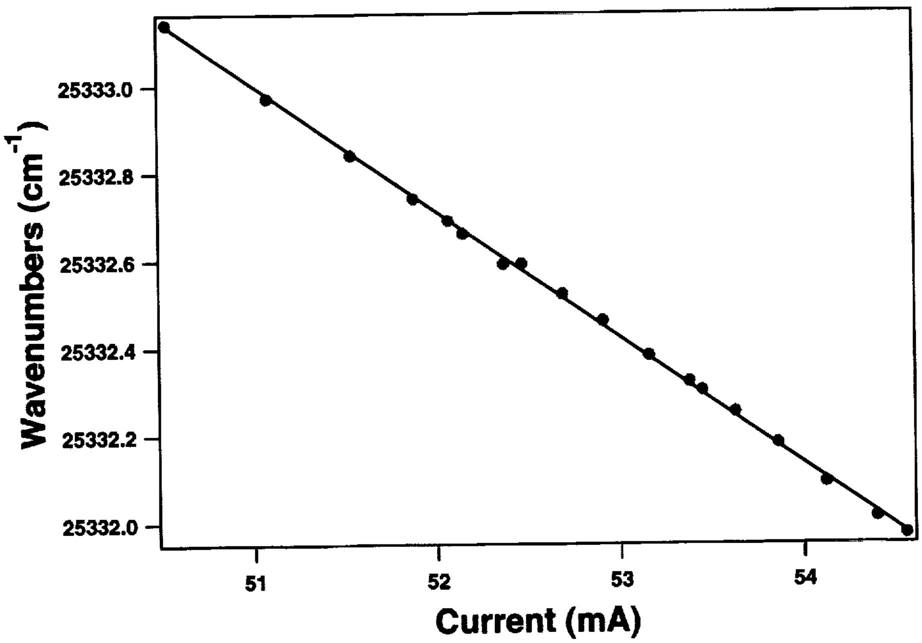

Figure 1- Wavelength tuning of the ECDL with diode laser injection current.

Incorporating the standard Fabry-Perot GaN laser into an external cavity allows recovery of the basic features that make a semiconductor device operating in the ultra-violet appealing for microgravity combustion diagnostics. Operation in an ECDL configuration allows inclusion of a separate wavelength-selective optical element that ensures operation at any desired wavelength within the device gain curve. We have constructed our ECDL around the well-known Littman-Metcalf[10] resonator. Fig. 2 shows a schematic diagram of the major components of this type resonator. In the Littman-Metcalf design the zeroeth order output of the diffraction grating is used as the laser output. The first order diffraction is retroreflected by a cavity feed back mirror which establishes one end of the resonator. The other end of the resonator is the outboard surface of the Fabry-Perot diode element. Wavelength selectivity is achieved by the angle of the diffracted return beam as determined by the cavity feed back mirror position.

PRESENT WORK

The goal of the present project is to develop a deliverable instrument for the quantitative detection of CH radicals in combustion studies and use this instrument in the 2.2 second drop tower at NASA Glenn Research Center. This instrument will be compatible with NASA Glenn microgravity drop tower facilities. The light source will consist of a frequency-agile, UV, external cavity diode laser that will be used to make high sensitivity line-of-sight absorption measurements.

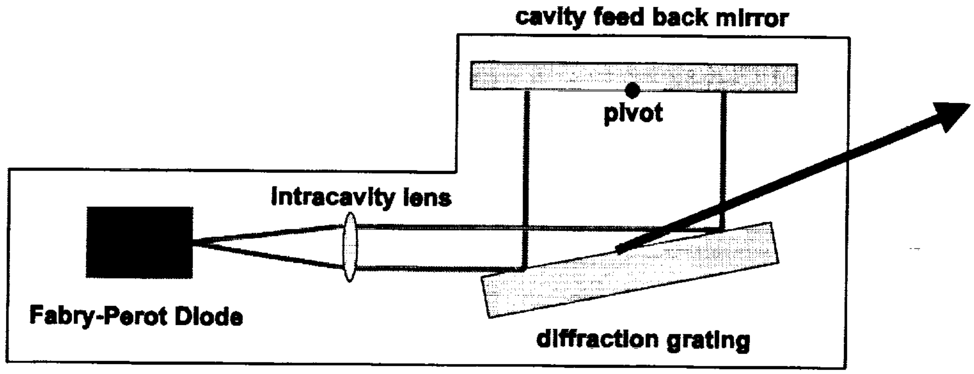

Figure 2 - A block diagram of a Littman-Metcalf external cavity diode laser.

This instrument will be compatible with our 1-D and 2-D imaging technology which we have utilized in previous NASA projects. We anticipate CH detection limits of 0.1 ppm over a 1 cm path and a spatial resolution of 0.5 mm with a 10 Hz measurement rate. Our present effort is directed toward optimizing the ECDL design for maximum wavelength tuning range with injection current and maximum wavelength modulation frequency. The basic optical elements are being engineered into an integrated and rugged package to withstand the rigors of the microgravity drop tower.

REFERENCES

1. D. B. Oh, A. C. Stanton and J. A. Silver, J. Phys. Chem. **97**, 2246 (1993).
2. D. B. Oh and A. C. Stanton, Appl. Opt. **36**, 3294 (1997).
3. J. A. Silver and D. C. Hovde, Rev. Sci. Instrum. **65**, 1691 (1994).
4. D. C. Hovde, T. P. Meyers, A. C. Stanton and D. R. Matt, J. Atmos. Chem., **20**, 141 (1995).
5. J. A. Silver, Appl. Opt., **31**, 707 (1992) and references therein.
6. D. S. Bomse, A. C. Stanton and J. A. Silver, Appl. Opt. **31**, 718 (1992) and references therein.
7. K. A. Peterson and D. B. Oh, Opt. Lett. **24**, 667 (1999).
8. J. A. Silver, D. J. Kane and P. J. Greenberg, Appl. Opt., **34**, 2787, (1995).
9. D. B. Oh, Opt. Lett., **20**, 101 (1995).
10. M. G. Littman and H. J. Metcalf, Appl. Opt. **17**, 2224 (1978).

This work is being performed under NASA Glenn Research Center contract NAS3-01007.