ROUTING AND ACTION

MEMORANDUM

ROUTING

TO:(1) Mechanical Sciences Division (Anthenien, Ralph)

Report is available for review

(2) Proposal Files   Report No.:   -RIP   Proposal Number: 65038-EG-RIP.2

DESCRIPTION OF MATERIAL

CONTRACT OR GRANT NUMBER: W911NF-14-1-0357

INSTITUTION: Stanford University

PRINCIPAL INVESTIGATOR: Ronald Hanson

TYPE REPORT: Final Report

DATE RECEIVED: 6/28/16 4:21PM

PERIOD COVERED: 7/1/14 12:00AM through 12/31/15 12:00AM

TITLE: Final Report: Laser-Based Alkene Sensors for Shock Tube Kinetics

ACTION TAKEN BY DIVISION

(x) Report has been reviewed for technical sufficiency and IS [x] IS NOT [ ] satisfactory.

(x) Material has been given an OPSEC review and it has been determined to be non sensitive and, except for manuscripts and progress reports, suitable for public release.

(x) Perfomance of the research effort was accomplished in a satisfactory manner and all other technical requirements have been fulfilled.

(x) Based upon my knowledge of the research project, I agree with the patent information disclosed.

Approved by NAE\RALPH.ANTHENIEN1 on 7/20/16 2:42PM

ARO FORM 36-E

REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

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13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT
We have acquired two laser-based alkene sensors for use in the investigation of fuel kinetics in shock tube experiments. These sensors operate at wavelengths between 10 and 12 microns in the far IR where there are strong absorption bands for a series of alkenes. The two sensors, operated together, can enable the detection of multiple key alkene products, including C2H4 and i-C4H8, that result from pyrolytic decomposition of hydrocarbon fuels. Kinetic analyses predict that alkenes form a large fraction of the decomposition products of jet fuels and jet fuel

15. SUBJECT TERMS
Shock tube, laser absorption, ethylene, iso-butene

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Ronald Hanson
UU	UU	UU	UU		19b. TELEPHONE NUMBER 650-723-6850

Report Title

Final Report: Laser-Based Alkene Sensors for Shock Tube Kinetics

ABSTRACT

We have acquired two laser-based alkene sensors for use in the investigation of fuel kinetics in shock tube experiments. These sensors operate at wavelengths between 10 and 12 microns in the far IR where there are strong absorption bands for a series of alkenes. The two sensors, operated together, can enable the detection of multiple key alkene products, including C2H4 and i-C4H8, that result from pyrolytic decomposition of hydrocarbon fuels. Kinetic analyses predict that alkenes form a large fraction of the decomposition products of jet fuels and jet fuel surrogates, and quantitative measurements using these laser systems have the potential to provide time-histories of the primary alkene decomposition products for such fuels. When employed on our existing shock tube test facilities with other existing laser-based species sensors, a substantially complete picture of the intermediate decomposition products that form during pyrolysis and oxidation should be feasible. These state-of-the-art sensors will also be used in the training and education of the next generation of graduate students in mechanical engineering in the areas of combustion, propulsion, laser diagnostics and shock tube methods.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u> <u>Paper</u>

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u> <u>Paper</u>

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Tom Parise	0.00	
FTE Equivalent:	**0.00**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Mitchell Spearrin	0.00
FTE Equivalent:	**0.00**
Total Number:	**1**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Ronald K Hanson	0.00	Yes
FTE Equivalent:	**0.00**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME	
Thomas Parise	
Total Number:	**1**

Names of personnel receiving PHDs

NAME	
Total Number:	

Names of other research staff

NAME	PERCENT_SUPPORTED
David F Davidson	0.00
FTE Equivalent:	**0.00**
Total Number:	**1**

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

Discussions of experience with EC-QCL, External Cavity - Quantum Cascade Lasers with a manufacturer (Block Engineering Marlborough MA 01752) to improve performance and usability of new product.

Final Report

Laser-Based Alkene Sensors for Shock Tube Kinetics

Fiscal Year 2014 Defense University Research Instrumentation Program (DURIP)

by

R. K. Hanson
Mechanical Engineering Department
Stanford University, Stanford CA 94305

Submitted to
Army Research Office
Engineering Sciences Directorate
Mechanical Sciences Research Program
Propulsion and Energetics Section
Dr. Ralph Anthenien Jr.

June 2016

Table of Contents

Abstract

We have acquired two laser-based alkene sensors for use in the investigation of fuel kinetics in shock tube experiments. These sensors operate at wavelengths between 10 and 12 microns in the far IR where there are strong absorption bands for a series of alkenes. The two sensors, operated together, can enable the detection of multiple key alkene products, including C_2H_4 and i-C_4H_8, that result from pyrolytic decomposition of hydrocarbon fuels. Kinetic analyses predict that alkenes form a large fraction of the decomposition products of jet fuels and jet fuel surrogates, and quantitative measurements using these laser systems have the potential to provide time-histories of the primary alkene decomposition products for such fuels. When employed on our existing shock tube test facilities with other existing laser-based species sensors, a substantially complete picture of the intermediate decomposition products that form during pyrolysis and oxidation should be feasible. These state-of-the-art sensors will also be used in the training and education of the next generation of graduate students in mechanical engineering in the areas of combustion, propulsion, laser diagnostics and shock tube methods.

Laser systems for alkenes

We have acquired two complementary sensor systems that can provide simultaneous measurement of two alkene species. In typical operation, the tunable 11 micron laser system is used to monitor one or more higher alkenes such as iso-butene, and a discretely tunable 10.5 micron system used to monitor C_2H_4. The equipment is currently being used in our shock tube facilities. A schematic of the two systems is shown in Fig. 1.

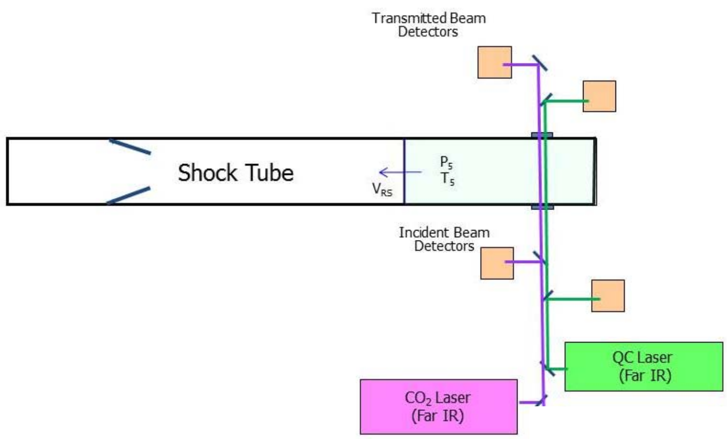

Figure 1. Schematic of a shock tube/laser absorption experiment for the detection of alkenes.

Tunable 11 micron laser system

The tunable 11 micron laser system is based around a Daylight Solutions tunable cw-pulsed quantum cascade laser. In addition, a matching pair of Boston Electronics Vigo thermo-electric cooled detectors (model PVI-2TE-5-2x2) are used to monitor, with common mode rejection, the absorbed laser signal, along with necessary beam-forming optics and windows.

Discretely-tuned CO_2 gas laser system

The discretely tunable CO_2 gas laser system for the detection of C_2H_4 is based around an Access Laser LASY-4G CO2 gas laser and with water chiller. This configuration maintains high output wavelength and power stability. Boston Electronics Vigo thermo-electric cooled detectors (model PVI-2TE-5-2x2) are used to monitor the absorption, along with necessary beam-forming optics and windows.

Detection of alkenes

The optical wavelength region near 10 microns features strong optical absorption transitions for many alkenes. Figure 2 shows room temperature spectra for several alkenes, C_2H_4, C_3H_6, i-C_4H_8 and the alkyne C_3H_4, between 850 and 1000 cm^{-1} or equivalently 10-11.76 microns. The absorption cross-sections for these species are significantly higher at these wavelengths than at the shorter wavelengths accessible by previously available commercial lasers. Though these absorption cross-sections are degraded at high temperatures, they are still strong enough to provide 10-100 ppm minimum detectivities for alkene species at combustion temperatures in shock tube/laser absorption experiments.

Unfortunately, the spectra of these species overlap, producing blended spectra during pyrolysis of real fuels. Our approach to dealing with this problem has been to utilize two separate lasers operating at different wavelengths, including one wavelength (from the CO_2 laser) chosen with maximum sensitivity to ethylene that is typically the dominant alkene formed. The second laser wavelength is chosen to optimize detection of a second alkene or blend of multiple large alkenes. Used together, the two wavelengths can enable detection of ethylene plus an additional alkene (or blend). Ideally, a third and even a fourth laser wavelength would be used; we tentatively plan that to be the basis of a new DURIP request in 2017.

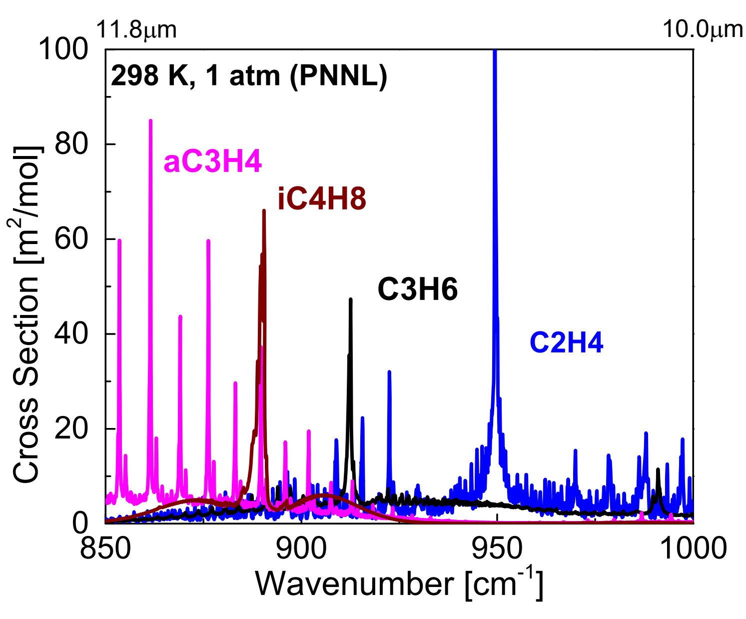

Figure 2. Absorption cross-sections for selected alkenes in the 850 to 1000 cm^{-1} region (10-11.76 μm). Data derived from the PNNL database.

As indicated above, ethylene can be monitored at 10.532 microns using an emission line of a CO_2 gas laser, as there is a fortuitous overlap of the strong Q-branch of the ν_7 ethylene band with the P14 line of the CO_2 laser transitions associated with the (001) to (100) vibrational levels. This strategy is based on the work in our laboratory by Ren et al. (W. Ren, D.F. Davidson and R.K. Hanson, "IR Laser Absorption Diagnostic for C_2H_4 in Shock Tube Kinetics Studies," Intl. J. Chem. Kinetics 44 (2012) 423-432 DOI 10.1002/kin.20599). For the detection of iso-butene, tunable laser light near 11 microns is used. This strategy is based on the work in our laboratory by Spearrin et al. (R.M. Spearrin, S. Li, D.F. Davidson, J.B. Jeffries and R.K. Hanson, "High-temperature Iso-butene Diagnostic for Shock Tube Kinetics using a Pulsed Quantum Cascade Laser near 11.3 μm," Proc. Comb. Inst. 35 3645-3651 (2015) DOI 10.1016/j.proci.2014.04.002).

Representative measurements using two alkene laser sensors

The two alkene laser sensors can be combined with an existing CH_4 detection scheme to provide the capability to measure three species simultaneously, as reported in a paper to be published in the Proceedings of the Combustion Institute (Vol.36). The target in that work was a novel three-color, three-species laser absorption sensor for measurement of small (C_2-C_4) alkenes. In that scheme, an existing two-color CH_4 laser sensor and one-color fuel sensor were combined with the two alkene sensors to study the decomposition of a bio-derived, highly-branched alcohol-to-jet (ATJ) test fuel in a shock tube, yielding multiple species (methane, ethylene, and isobutene) time-histories for temperatures between 1070 K and 1320 K. A matrix analysis scheme enabled the de-convolution of the multiple laser signals into species time-histories. Figure 3 shows representative species time-histories for three target species based on the measured absorbance signals.

Owing to the successful deployment of a three-laser sensor for ATJ fuels, we plan to propose acquisition of another tunable 11 micron laser in the 2017 DURIP program, thereby expanding our capabilities for studies of distillate fuels.

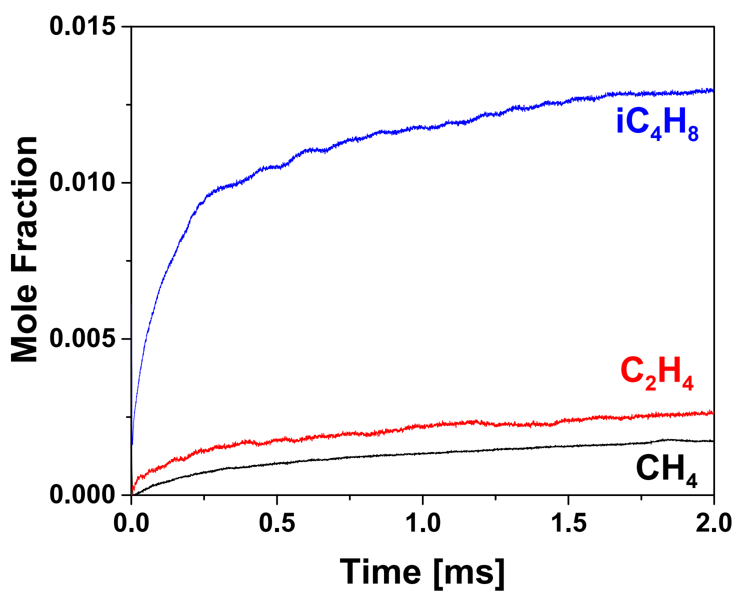

Figure 3. Species time histories during ATJ fuel pyrolysis. Initial reflected shock conditions: 0.917% C1 test fuel in argon, 1176 K, 1.40 atm.

Research facilitated

The overall goal of acquiring these lasers was to enable experiments that provide a more complete description of the intermediate product distribution of fuels and surrogate components of interest to ARO and other DOD research groups. Using this equipment, we were able to begin to quantify the decomposition product distributions of JP-8 and other jet fuel analogs, including bio-derived alternatives.

This equipment was used in the ARO research contract "Studies of ARO-Relevant Fuels using Shock Tube/Laser Absorption Methods," Grant # W911NF-13-1-0206, enabling an expansion of the current database of kinetics targets for ARO-relevant fuels.

Other DOD and U.S. government department contracts have also directly benefitted from the acquisition of this new equipment. These contracts include:

AFOSR/BRI: "New approaches to reacting flow modeling for endothermic fuel cracking and Combustion in high-speed combustion," October 2012-September 2015; funding level of $225k/year

DOE: "Spectroscopy and kinetics of combustion gases at high temperatures," March 2012-February 2015; funding level of $160K/year.

Effect on graduate education

This equipment will serve to benefit the training and education of the next generation of graduate students in mechanical engineering in the areas of combustion, propulsion, laser diagnostics and shock tube methods. The greater portion of the graduate students who have pursued higher degrees, M.Sc. and Ph.D., under the supervision of Professor R. K. Hanson at Stanford University have done so with the support of DoD funding. (Over 100 students have received Ph.D. degrees from the Hanson group.) Several of these students have learned to develop and use state-of-the-art laser diagnostic and spectroscopic techniques, to design and use shock tube facilities, and to apply these tools to studying current combustion problems of interest to the DoD. Many of the graduating students have gone on to become professors in their own right (28 at current count). Other students using this equipment will be trained in new scientific methods and able to pursue careers as leaders in science and engineering in the United States.