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Broadly Tunable Mid-Infrared Hydrocarbon Sensor

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Project Overview

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- **Project description**
  - Technical approach: use frequency mixing of near-infrared diode lasers to generate broadly tunable mid-infrared radiation, perform laser spectroscopy on a sample of the process gas to provide real-time species information which will be used to control the process
- **Objectives (*Phase I* and Phase II)**
  - *Obtain FTIR spectra, choose target gas*
  - *Design, fabricate first-generation frequency mixer chip*
  - *Measure laser performance in mid-IR*
  - *Develop conceptual design of laser spectrometer*
  - Optimize design of frequency mixer chip
  - Design, fabricate portable prototype gas analyzer
  - Demonstrate speciation in the laboratory
  - Demonstrate speciation in a petrochemical facility
- **Overall goal**
  - To develop a prototype broadly tunable mid-infrared laser gas analyzer which can be used in the petrochemical industry for process control and environmental monitoring

Technical Merit

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- **Addresses technical need(s) of the S/C community and the S/C priorities of the IOFs**
  - Portable gas analyzer can be placed close to the process stream
  - Relative species concentrations can therefore be measured in seconds, used to control the process in real time
  - The result is a more efficient process: higher yield of the desired product mix
  - Concept was developed for ethylene manufacturing, can also be applied to manufacturing of ETO, polyethylene, VCM, and other species containing carbon-hydrogen bonds
  - Gas analyzer can also be used for exposure monitoring: ETO, formaldehyde, benzene, etc.

Technical Merit

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- **Contributes new information or technology to the S/C community**
  - Existing gas analyzers (e.g. gas chromatograph, FTIR) are located far from process stream, leading to a significant delay time (minutes)
  - Measured species concentrations can't be used to control the process in real time
  - Proposed gas analyzer represents a significant advance, by measuring species concentrations in seconds rather than minutes

Technical Progress and Outlook

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Major progress/accomplishments to date *(Phase I)*

- *FTIR spectra of several industrially important target gases acquired; mixture of hydrocarbons chosen for further study*
- *Frequency mixer chips designed and fabricated, all show adequate mixing efficiency (~1%/W); information needed to improve the mixing efficiency obtained*
- *Laser source tunable over 250 cm^{-1}, narrowband enough to resolve pressure-broadened lines of methane; first demonstration of broadly-tunable mid-IR generation using this type of mixer chip*
- *Conceptual design for Phase II instrument created*
- *All Phase I objectives were achieved*
- *Additional objective achieved: absorption spectrum of industrially important hydrocarbon mixture obtained using broadly tunable laser source, showing that speciation of this mixture is possible*

Demonstration of Laser Tuning Range

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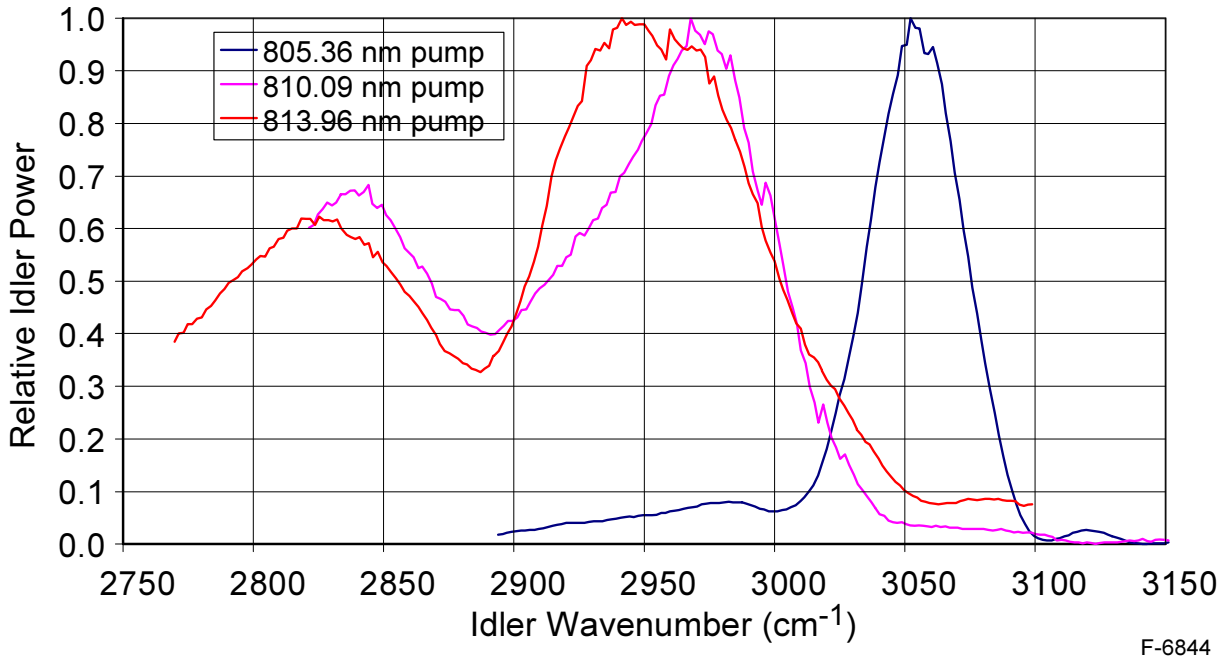
- **Tuning of ~250 cm^{-1} demonstrated with proper choice of the near-infrared wavelengths going into frequency mixer and the temperature of the mixer chip**
- **Unexpected dip observed in middle of tuning range; power normalization needed**



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- **Proof of feasibility: broad tuning can be achieved in this type of mixer chip**

Absorption Spectrum: Hydrocarbon Mixture

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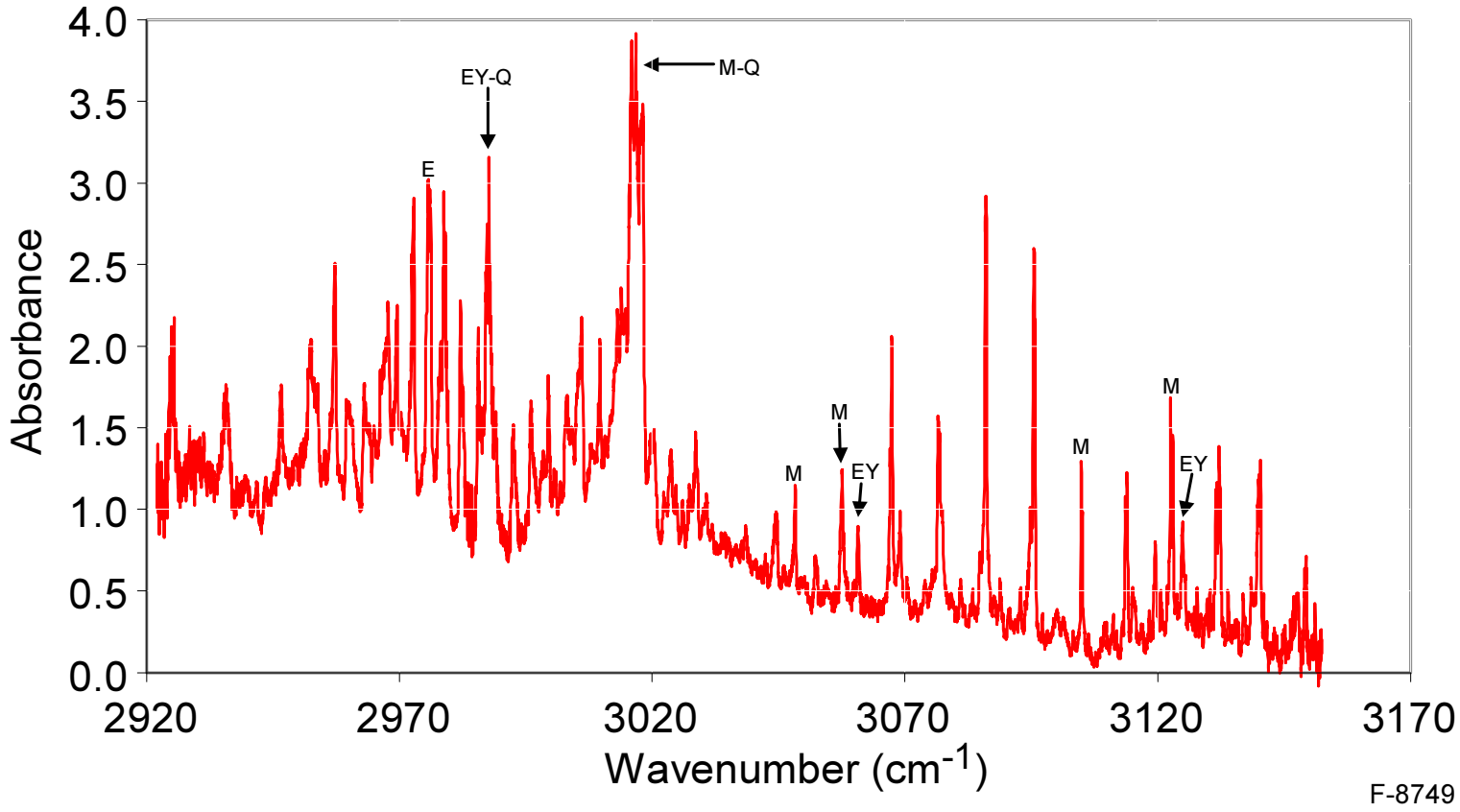
- **2.8% CH_4 (M), 9.3% C_2H_4 (EY), 4.9% C_2H_6(E), balance N_2, 772 Torr**



- **Further proof of feasibility: speciation is possible**

Gas Analysis Result: Hydrocarbon Mixture

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Species	Line Position (cm^{-1})	Calculated Fraction (from Peak Height)	Certified Fraction (from Manufacturer)
Methane	3105	17.4%	16.5%
Ethane	2976	31.1%	28.8%
Ethylene	3125	51.5%	54.7%

- **Good agreement using simple measurement of three peak heights (3 data points out of 10,000)**
- **Tradeoff between measurement accuracy and measurement speed will be addressed during Phase II**

Technical Progress and Outlook

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Future Technical Milestones/Goals (Phase II-Pending)

Milestone/Goal	Expected Completion Date	Comments
Design, Fabricate, Test Improved Frequency Mixer Chip	March 2004	Improve mixing efficiency from 1%/W to 5%/W
Design, Fabricate, Test Prototype Gas Analyzer	October 2004	Build portable instrument
Demonstrate Speciation in Laboratory	January 2005	Measure calibrated mixtures, optimize detection strategy
Demonstrate Speciation in Petrochemical Facility	June 2005	Measure process gases at Dow Freeport facility
Project Completion	July 2005	Assumes July 2003 start date

Technical Progress and Outlook

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Expected progress toward milestones/goals

- **Increase mixing efficiency from 1%/W to 5%/W by improving design of mixing chip; Phase I results provided the needed design information**
- **Develop portable instrument the size of a small suitcase: previous NASA-funded programs have produced DFG-based spectrometers this small**
- **Demonstrate speciation of an industrially significant gas mixture in the laboratory: Phase I results show feasibility, but tests under more realistic conditions are needed**
- **Demonstrate speciation in a petrochemical facility: interface between the instrument and the process must be established; logical extension of existing PSI gas analyzers based on absorption in the near-infrared**
- **Possible barriers: efficiency of mixing chip, ruggedness of portable instrument, spectral interference, system cost: all will be addressed in Phase II**

Technical Progress and Outlook

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Industrial end-user involvement

- **PSI will work with Analytical Specialties Inc. (ASI) to develop and test prototype HC process analyzers**
- **ASI is already a licensee of PSI near-IR TDL sensor technology for NO_x emissions control as a result of a previous DoE STTR program**
- **ASI is the leading supplier of TDL-based gas analyzers in the US**
- **ASI's principal business is specialized analyzers for the US petrochemical industry and is headquartered in Houston, TX**
- **Dow will provide information about chemometric analysis schemes**

ASI provides unique access to important, unmet petrochemical analyzer needs

- process definition
- sensor specifications, packaging, environmental requirements
- access for prototype testing in Phase II at Dow Chemical

Market Potential

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- **Commercialization plan**
  - Potential market sizes, desirable performance specifications and price points have been identified for the hydrocarbon sensor
  - Our general strategy is to work with entrenched suppliers for target industries (e.g. ASI $\rightarrow$ petrochemical)
  - Existing ASI/PSI Near-IR sensor product provides a useful precedent
  - Prototype testing, and consideration of market needs, will take place early (during Phase II)

Market Potential

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- **Other IOF areas of applicability**
  - Any chemical species containing carbon-hydrogen bonds is a potential target of this sensor; wide applicability in petrochemical industry
  - Examples within petrochemical industry include manufacturing of ethylene oxide, polyethylene, vinyl chloride monomer
  - Exposure monitoring (e.g. ethylene oxide, formaldehyde, benzene) can benefit industry by lowering safety-related costs
  - Other industries can benefit: e.g. monitoring removal of solvents in pharmaceutical manufacturing

- **After OIT project completion, what's next?**
  - Work with ASI to develop a commercial product based on this technology
  - Access to facilities at Dow (e.g. the Freeport facility) will be provided for prototype testing during product development

Programmatic Merit

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- **Energy benefits**
  - Improved process efficiency will decrease the amount of starting material needed
  - Decreased starting material amount can be translated into energy and cost savings
  - Estimated annual energy savings: 3×10^{11} BTU (3×10^{5} kW-hr) at Dow Freeport facility, 5×10^{12} BTU (5×10^{6} kW-hr) for all US hydrocarbon-cracking facilities
- **Economic and environmental benefits**
  - Improved process efficiency increases profitability for petrochemical companies
  - Indirect benefit to environment from decreased energy consumption

Summary

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- **Successful Phase I program: all technical objectives achieved, along with an additional measurement on an industrially important hydrocarbon mixture**
- **Two key risks overcome: source based on frequency mixing chip does have the predicted wide tuning range, industrially important hydrocarbon mixture can be speciated using this source**
- **Phase II program will produce a prototype gas analyzer and support testing by Dow/ASI in a petrochemical facility**
- **Gas analyzer will be used by ASI/Dow to increase efficiency of hydrocarbon cracking process for ethylene production, has potential use for several other manufacturing processes**

ACKNOWLEDGMENT

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