SHOCK TUBE CHARACTERIZATION OF LASER ABSORPTION SENSORS FOR COMBUSTION MEASUREMENTS OF GREEN PROPELLANTS

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ABSTRACT

Chemical kinetic models for green spacecraft propulsion systems are needed to calculate efficiency, estimate toxic products, and mitigate plume impingement risks. Laser absorption spectroscopy (LAS) is a common technique used to measure time-resolved mole fraction for model validation. LAS was used to measure species-time history nitrous oxide (N_2O) and carbon monoxide (CO) behind reflected shock waves. The diagnostics were implemented at the University of Central Florida high-pressure shock tube facility. A mixture of ethylene (0.002) and N_2O (0.008) was diluted with argon gas (0.99) and shock heated 12 bar and temperatures from 1400 to 1600 K.

INTRODUCTION

Hydrazine has been used as a spacecraft propellant for decades. Starting in the 1950s, hydrazine was first used by the Jet Propulsion Lab in the Titan rocket propulsion system [1]. In a 1971 technical report released to the public, a trade study was conducted to determine the best propulsion system for keeping satellites in orbit. Silverman [2] compared ionic thrusters, a colloid thruster, and hydrazine monopropellants. Several factors were compared including performance, mass, and cost. At the time, it was concluded that the hydrazine monopropellant propulsion system was ideal for orbital maintenance. In the late 1970s, a propulsion system using hydrazine with a Shell 405 catalyst was successfully used in space exploration missions to Mars [3].

Hydrazine bipropellant propulsion systems were used for the Space Shuttle Orbiter, which was an application with a high specific impulse requirement. In a comprehensive review on the history of hydrazine, Schmidt [1] stated that the specific impulse of hydrazine monopropellant is 2313 N s/kg and the bipropellant combination with nitrogen tetroxide is 38% higher. Due to the toxicity and carcinogenic nature of the propellant, non-toxic propellants for spacecraft maneuvering became a topic of interest. The OSHA limit on human exposure to hydrazine is 1 ppm per eight-hour workday. Designs were proposed to replace the hydrazine reaction control system on the space shuttle with liquid oxygen and ethanol to improve the safety and cost of the system [4]. Two decades later, the use of hydrocarbon and LOX propellant combinations has become popular in the development of launch vehicles. There are also efforts to develop hydrocarbon bipropellant spacecraft maneuvering systems. For example, The German Aerospace Center has developed and fired a 1 N and 22 N bipropellant thruster using the propellant blend termed, “HyNOx”. The blend includes hydrocarbons such as ethylene, ethane, and nitrous oxide [4].

Hydroxylammonium Nitrate (HAN) based monopropellants also became a topic of research for new spacecraft propulsion systems. In a review paper, Jankovsky [5] stated that a recent study by NASA calculated the amount of hydrazine and HAN propellant needed to complete the same mission. It was found that the use of HAN would reduce the mass of fuel needed by 17.5%. It was estimated through a one-dimensional equilibrium code that HAN based propellants have a higher specific impulse and storage density compared to a nitrogen tetroxide monopropellant. It was concluded that a redesign of heritage monopropellant systems would be justified for the reduced cost and lower toxicity of HAN based propellants. Recently, NASA demonstrated ionic green propellant technology during the Green Propellant Infusion Mission (GPIM). For this mission, Aerojet Rocketdyne designed a 22 N ASCENT thruster that was flown during the mission. McLean et al [4] noted that the propellant loading procedures were relaxed compared with hydrazine propellants by Range Safety after an assessment done on the propellant risks. The NASA Glenn Research Center assessed the ASCENT plume impingement risks by measuring the exhaust temperature and chemical species mole fractions in a vacuum chamber. Raman Spectroscopy was employed as an optical diagnostic to obtain the desired measurements. However, expected species in the exhaust such as hydrocarbons and NOx compounds could not be differentiated. The measured plume temperature was compared with reactive computational fluid dynamics simulations. It was found that the predicted temperature was 300 K lower than what was measured using Raman Spectroscopy.

For green spacecraft propulsion technology to mature, improvements need to be made to the quality of chemical kinetic models used in computational fluid dynamics simulations. Further chemical kinetics research will have benefits to both combustion chamber and plume impingement risk assessment resulting in better efficiency and safety of the mission. The chemistry of HAN based propellants has been studied in calorimeters and with mass spectroscopy. Lee and Litzinger [6] employed Fourier Transform InfraRed (FT-IR) Spectroscopy to measure the thermal decomposition of HAN. The species detected during decomposition included H_2O, N_2O, NO, NO_2, and HNO_3. Esparza [7] confirmed these species and NO_2 during an experimental campaign on the thermal decomposition of HAN propellant using techniques including FT-IR, differential scanning calorimetry, and mass spectrometry. Amrousse et al. [8] measured burning rates of HAN propellants and tested two different catalysts in a 20 N thruster.

The combustion of hydrocarbons has been studied extensively. However, available literature on the combustion of hydrocarbons with NOx is limited. There have been recent studies that measure the hydrocarbons with NO_2 oxidizer ignition delay time, or how long it takes for a mixture at elevated temperature and pressure to ignite [9-12]. This parameter is critical for assessing the validity of theoretical chemical kinetic models. However, to propose changes to a given chemical kinetic mechanism further data is required such as species time-history. Mathieu et al. [13] measured carbon monoxide (CO) mole fraction in a shock tube study of NO_2, CH_4 and C_2H_6. Zheng et al [14] measured CO, CO_2, H_2O, NH_3, and NO mole fraction and IDT during shock tube experiments with CH_4, H_2, NH_3, and C_2H_4. Yang [15] measured nitrous oxide and ethylene ignition delay times in a rapid compression machine. Janzer et al. [16] measured the ignition delay time of N_2O mixtures with ethane and ethylene in a shock tube. Speciation measurements are needed for hydrocarbon and N_2O mixtures at spacecraft propulsion relevant conditions. In this work, species-time history of N_2O and CO were measured behind reflected shock waves. A mixture of ethylene (0.002) and N_2O (0.008) was diluted with argon gas (0.99) and shock heated 12 bar and temperatures from 1400 to 1600 K. The time-resolved mole fraction data will be compared to the NUIG 1.2 chemical kinetic mechanism [17].

BACKGROUND

Laser absorption spectroscopy (LAS) is an optical diagnostic used to take in-situ measurements of combustion species mole fractions. The technique is governed by the Beer Lambert law, shown in Equation 1 which relates the ratio of transmitted to attenuated light at a given wavelength to mole fraction. This calculation requires the absorption cross-section, σ to be characterized at the measurement conditions. The HITRAN [18] and HITEMP [19] databases are commonly used to determine the cross-section value. However, these databases need to be validated at elevated temperature and pressure. Shock tube facilities are commonly used for these measurements due to their well-defined thermodynamic states.

$$\alpha = -\ln\left(\frac{I}{I_0}\right) = \frac{\sigma P L X}{RT} \qquad [1]$$

A quantum cascade laser at 4.6 µm was used to measure N_2O decomposition during shock tube experiments. At this wavelength, CO is absorbed as well. To resolve the N_2O mole fraction, an additional laser was used to measure CO at 4.9 µm. Figure *1*. shows the 4.9 µm laser schematic used to detect the laser signal. Gold plated mirrors are used to direct the laser through the shock tube test section. The test section has eight optical ports with 1-inch windows located 1-cm from the end wall. Before entering the shock tube, the laser beam is split and directed to a reference detector (Vigo MIP-DC-5M-F-M4) to account for power fluctuations. A Bristol Spectrum Analyzer is used to check the wavelength of the laser. After passing through the shock tube, to mitigate interference from emissions, a 5040-155 nm bandpass filter was placed before the transmitted signal detector (Vigo MIP-DC-6M-F-M4). A neutral density filter was used to reduce the laser signal, due the detector to reach its maximum voltage reading.

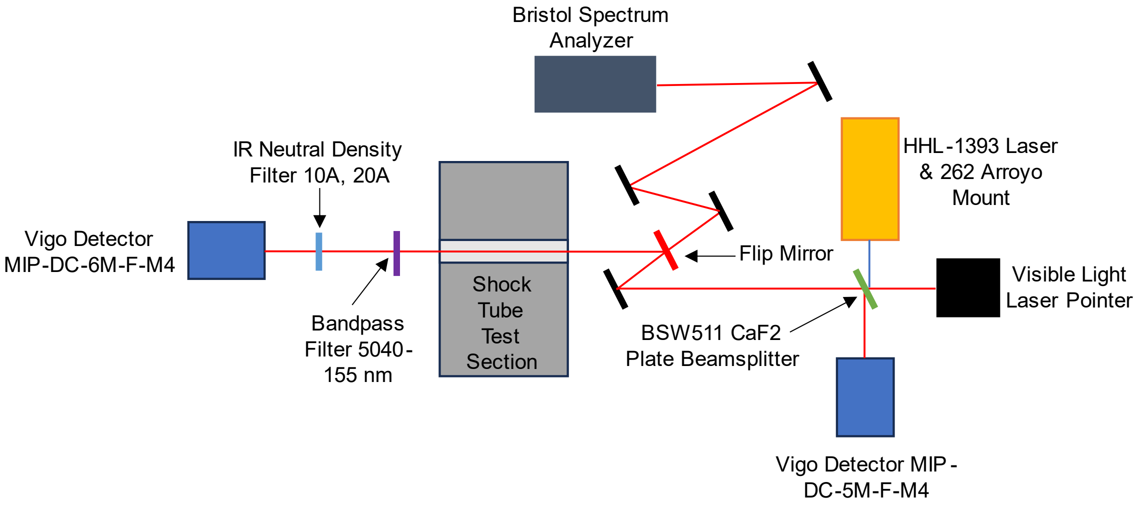

Figure 1. 4.9 µm Laser Schematic

EXPERIMENTAL METHODS

The measurements were conducted in the High-Pressure Extended Range Shock Tube Facility, which has been previously described in Urso et al [20]. Two MKS Baratron capacitance manometers were used to fill the mixture constituents to the required partial pressure in a stainless-steel mixing tank. Argon gas was used as the mixture diluent. The partial pressure of argon gas was measured by the high-pressure manometer which is rated for 20,000 Torr (627F24TBC1B). The partial pressure of C_2H_4 and N_2O to 100.00 Torr (627F12TBC1B). Both had an accuracy of 0.12% of reading. The gases were stirred for at least one hour to ensure homogeneity of the mixture. Before each experiment, the shock tube was vacuumed down to a pressure below 9e-6 torr by a turbomolecular pump (Agilent TwisTorr 305S). This procedure removes impurities from the ambient air initially in the shock tube that would disrupt the mixture concentration. A Lesker (KJLC354401YF) ion gauge was used to read the final vacuum pressure of the shock tube before filling the mixture.

The shock tube was separated into two sections by a 0.063-inch-thick aluminum diaphragm. The driven side was filled with a mixture to an initial pressure P1. The driver side was filled to a pressure P4 with a tailored mixture of nitrogen and helium to achieve a relevant P5 and T5 condition. To ensure that the diaphragm will break at the desired P4, it was scored with a cross shape to a pre-selected depth by a Bantam CNC Mill. The incident shock Mach number was calculated by Agilent timer-counters (53220A) at known axial distances from the end wall. The timer-counters were connected with piezoelectric pressure transducers that measure the dynamic pressure during the experiment for comparison with the ideal normal shock equations. The thermodynamic state of each experiment is resolved by using the measured initial pressure ratio across the diaphragm and the speed of the incident shock wave assuming frozen chemical equilibrium. Experimental data was acquired by an NI PCIe-6376 DAQ at a rate of 2.5 MHz per channel.

RESULTS AND DISCUSSION

Figure 2 shows preliminary time resolved N_2O mole fraction data at 12.5 bar and 1413.7 K. The absorption cross-section of N_2O at 4.9 µm and 4.6 µm was calculated within the first few microseconds of the experiment before decomposition begins and the concentration is known. The uncertainty in mole fraction was calculated using the root sum square method. The facility uncertainty in temperature and pressure have been previously characterized [20]. Uncertainty in the absorbance was calculated from the signal to noise ratio of each laser from an inert shock tube experiment. These parameters also were used to determine the uncertainty in absorption cross-section for N_2O at 4.6 µm and 4.9 µm. After 1 millisecond, interference from CO becomes significant and interferes with N_2O at 4.6 µm. Preliminary cross-section measurements were conducted for both CO and N_2O. The measured trends showed agreement with HITEMP and HITRAN respectively, but further data needs to be collected to confirm the initials data collected. The cross-sections from HITRAN and HITEMP need to be further validated in future work, so the data past 1 millisecond is not reported here. The N2O-time history was compared with the NUIG 1.2 mechanism plotted blow in red. After 0.6 milliseconds, NUIG 1.2 predicts a faster decay in mole fraction compared with the measured data.

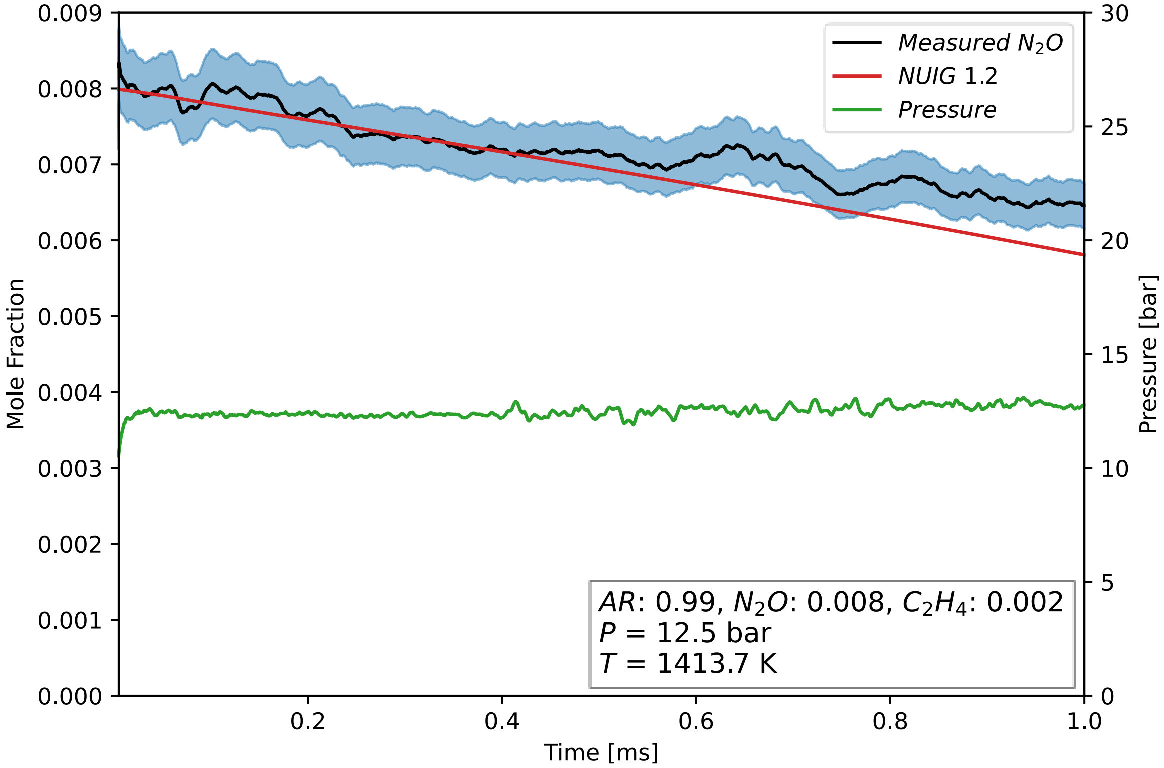

Figure 2. N_2O Mole Fraction Data

SUMMARY AND CONCLUSIONS

LAS of was used to measure species-time history of N_2O and CO behind reflected shock waves. The diagnostics were implemented at the University of Central Florida high-pressure shock tube facility. A mixture of C_2H_4 (0.002) and N_2O (0.008) was diluted with argon gas (0.99) and shock heated 12 bar and temperatures from 1400 to 1600 K.

FUTURE WORK

In future work, cross-sections of CO at 4.6 µm and 4.9 µm will be further validated in the University of Florida shock tube facility. The effects of nitric oxide (NO) addition, an intermediate product during green propellant combustion, will be measured. The mole fraction of nitric oxide will be measured with a 5.2 quantum cascade laser. The baseline results from the present work will be compared to the mixture with nitric oxide addition. The results will serve to identify sensitive reactions in the NUIG 1.2 mechanism that need to be further studied to improve the mechanism.

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REFERENCES

[1] E. Schmidt, "One hundred years of hydrazine chemistry," in *3rd conference on the environmental chemistry of hydrazine fuels, Florida*, 1987.

[2] R. V. Silverman, "An Evaluation of Electric and Hydrazine Propulsion Systems for Orbit Maintenance," NAVY SPACE SYSTEMS ACTIVITY LOS ANGELES CA, Defense Technical Information Center, 1971 Apr 01.

[3] D. MORRISEY, "Historical perspective - Viking Mars Lander propulsion," in *25th Joint Propulsion Conference*.

[4] E. Hurlbert, J. Applewhite, T. Nguyen, B. Reed, Z. Baojiong, and W. Yue, "Nontoxic orbital maneuvering and reaction control systems for reusable spacecraft," *Journal of Propulsion and Power,* vol. 14, no. 5, pp. 676-687, 1998.

[5] R. S. Jankovsky, "HAN-based monopropellant assessment for spacecraft," 1996.

[6] H. Lee and T. A. Litzinger, "Thermal decomposition of han-based liquid propellants," *Combustion and Flame,* vol. 127, no. 4, pp. 2205-2222, 2001/12/01/ 2001, doi: https://doi.org/10.1016/S0010-2180(01)00322-4.

[7] A. Esparza, "Thermoanalytical Studies On The Decomposition Of Energetic Ionic Liquids," Ph.D., Mechanical Engineering, University of Texas El Paso, Open Access Theses & Dissertations, 2020-01-01.

[8] R. Amrousse *et al.*, "New HAN-based mixtures for reaction control system and low toxic spacecraft propulsion subsystem: Thermal decomposition and possible thruster applications," *Combustion and Flame,* vol. 162, no. 6, pp. 2686-2692, 2015/06/01/ 2015, doi: https://doi.org/10.1016/j.combustflame.2015.03.026.

[9] F. Deng *et al.*, "Towards a kinetic understanding of the NOx sensitization effect on unsaturation hydrocarbons: A case study of ethylene/nitrogen dioxide mixtures," *Proceedings of the Combustion Institute,* vol. 37, no. 1, pp. 719-726, 2019.

[10] A. A. E.-S. Mohamed, S. Panigrahy, A. B. Sahu, G. Bourque, and H. Curran, "The effect of the addition of nitrogen oxides on the oxidation of ethane: An experimental and modelling study," *Combustion and Flame,* vol. 241, p. 112058, 2022.

[11] F. Deng, H. Xu, X. Liu, Y. Wu, H. Zheng, and Z. Li, "Effect of nitrogen dioxide addition on ethane auto-ignition at different pressures and equivalence ratios: Experiments and chemical kinetic modeling," *Fuel,* vol. 285, p. 119042, 2021.

[12] T. Newman-Lehman, R. Grana, K. Seshadri, and F. Williams, "The structure and extinction of nonpremixed methane/nitrous oxide and ethane/nitrous oxide flames," *Proceedings of the Combustion Institute,* vol. 34, no. 2, pp. 2147-2153, 2013.

[13] O. Mathieu, S. P. Cooper, S. A. Alturaifi, and E. L. Petersen, "Assessing NO2-Hydrocarbon Interactions during Combustion of NO2/Alkane/Ar Mixtures in a Shock Tube Using CO Time Histories," *Fuels,* vol. 3, no. 1, pp. 1-14, 2022. [Online]. Available: https://www.mdpi.com/2673-3994/3/1/1.

[14] D. Zheng *et al.*, "Experimental study of the methane/hydrogen/ammonia and ethylene/ammonia oxidation: Multi-parameter measurements using a shock tube combined with laser absorption spectroscopy," *Combustion and Flame,* vol. 254, p. 112830, 2023/08/01/ 2023, doi: https://doi.org/10.1016/j.combustflame.2023.112830.

[15] M. Yang, X. Ma, Z. Huang, and C. Tang, "Role of O2 on nitrous oxide fuel blend ethylene auto-ignition sensitivity," *Combustion and Flame,* vol. 259, p. 113167, 2024.

[16] C. Janzer, S. Richter, C. Naumann, and T. Methling, "“Green propellants” as a hydrazine substitute: experimental investigations of ethane/ethene-nitrous oxide mixtures and validation of detailed reaction mechanism," *CEAS Space Journal,* vol. 14, no. 1, pp. 151-159, 2022.

[17] A. B. Sahu *et al.*, "An experimental and kinetic modeling study of NOx sensitization on methane autoignition and oxidation," *Combustion and Flame,* vol. 238, p. 111746, 2022/04/01/ 2022, doi: https://doi.org/10.1016/j.combustflame.2021.111746.

[18] I. E. Gordon *et al.*, "The HITRAN2016 molecular spectroscopic database," *Journal of Quantitative Spectroscopy and Radiative Transfer,* vol. 203, pp. 3-69, 2017/12/01/ 2017, doi: https://doi.org/10.1016/j.jqsrt.2017.06.038.

[19] L. S. Rothman *et al.*, "HITEMP, the high-temperature molecular spectroscopic database," *Journal of Quantitative Spectroscopy and Radiative Transfer,* vol. 111, no. 15, pp. 2139-2150, 2010/10/01/ 2010, doi: https://doi.org/10.1016/j.jqsrt.2010.05.001.

[20] J. J. Urso *et al.*, "Characterization of a new ultra-high pressure shock tube facility for combustion and propulsion studies," *Review of Scientific Instruments,* vol. 93, no. 6, 2022, doi: 10.1063/5.0084047.