Multispecies Absorption Measurements in an Ammonium Dinitramide based Thruster

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A combined near-infrared and mid-infrared laser-based absorption sensor is developed for simultaneous measurements of \(N_2O, CO, NO\) and gas temperature for a 1-Newton ADN monopropellant thruster. ADN monopropellant represents a new generation of green propellant for spacecraft propulsion and goes with developing ADN based thruster. An optimization design for an ADN based thruster with catalytic bed length of 14 mm is studied in this paper. Both steady-state firing and pulse-mode firing for the ADN based thruster operation are conducted over feed-pressure range of 5-12 bar at ignition temperature of 200 °C. Scanned-wavelength direct absorption is utilized to measure the multispecies concentration and gas temperature under the firing conditions. Measurements employing the developed laser-based absorption sensor provide an access to characterize the combustion process inside the ADN based thruster. Additional measurements for the combustion pressure are made by using a high-temperature resistant and high frequency pressure sensor.

**Nomenclature**

\(A\) = integrated absorbance

\(I_0\) = incident spectral intensity, \(W/cm^2 s\)

\(I_t\) = transmitted spectral intensity, \(W/cm^2 s\)

\(L\) = optical path length, cm

\(P\) = pressure, atm

\(X_{abs}\) = mole fraction of absorbing species

\(S(T)\) = transition linestrength, \(cm.molecule^{-1}\)

\(T\) = temperature, K

\(\nu\) = laser tuning frequency, \(cm^{-1}\)

\(\nu_0\) = line center frequency, \(cm^{-1}\)

\(\phi(\nu-\nu_0)\) = lineshape function

**I. Introduction**

Recently, green space propulsion has become a common goal for small-satellite propulsion by using non-toxic monopropellants, in which a new green liquid monopropellant based on ammonium dinitramide (ADN) have been developed for spacecraft propulsion\(^[1]\). ADN monopropellant is a liquid blend of high energetic oxidizing ADN (NH\(_4\)(NO\(_2\))\(_2\)), water and fuel methanol \(^[2]\). Owing to higher performance, lower toxicity and safer handling of the monopropellant, ADN based thruster has great potential to replace the hydrazine thruster in small satellite missions, while the developments of ADN liquid monopropellant for spacecraft propulsion have been discussed in the previous studies \(^[1, 3-5]\). Successful in-space demonstration of the High Performance Green Propulsion (HPGP) system based on a 1 N ADN based thruster have been implemented on the PRISMA spacecraft platform \(^[4-7]\).

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It is essential to understand the combustion process of ADN monopropellant so as to improve performance of the thruster. Theoretically, the combustion mechanism of ADN monopropellant is currently being studied. Most researchers divide this process into decomposition and combustion, and a mechanism has been proposed for decomposition reactions that involves two branches [8-11]. Fig. 1 presents the detailed decomposition and combustion processes of ADN monopropellant. Key reaction intermediates like N$_2$O and NO generate by ADN decomposition and reduce by combustion, while CO stands for a typical products of methanol-related combustion reactions and represents the combustion degree. Therefore, diagnostic of multispecies provide an access to characterize the combustion process in the ADN based thruster.

Traditional diagnostic methods are disadvantageous for in situ measurements due to long response time and intrusion into flow field, while a new non-intrusive method based on laser absorption spectroscopy is suitable for ADN combustion diagnostics and applied in this paper. For measurements for ADN based thruster hot firing test, a laser based diagnostic system is developed by combining mid-IR absorption sensor and near-IR absorption sensor. Mid-IR quantum cascade laser (QCL) absorption spectroscopy is used to detect the concentration of N$_2$O, NO, CO in the thruster chamber, while the gas temperature is measured by near-IR diode absorption sensor. Preliminary measurements for N$_2$O and gas temperature in a similar thruster have been presented in [12].

![Decomposition and combustion process of ADN monopropellant](image_url)

**II. Absorption spectroscopy and Methodology**

Laser absorption spectroscopy for molecular monochromatic transition at frequency $v$ is expressed by the Beer–Lambert law, which the relation between the transmitted intensity $I_t$ through gas medium of optical path length $L$ (cm) and the incident intensity $I_0$ can be expressed as shown in Eq. (1).

$$\frac{I_t}{I_0} = \exp(-\alpha_v)$$

where $\alpha_v$ represents the spectral absorbance coefficient. For an isolated transition $i$,

$$\alpha_v = PXS(T)\phi(v-v_0)L$$

Where $P$ (atm) is the pressure, $X$ is the mole fraction of the target absorbing species, $S(T)$(cm$^2$atm$^{-1}$) is the line strength of the transition at specific temperature $T$ (K), and $\phi(v-v_0)$ (cm) the line shape function at wavelength center of $v_0$. The line-shape function $\phi(v-v_0)$ is normalized such that \( \int_{-\infty}^{+\infty} \phi(v-v_0)dv = 1 \) and the integrated absorbance (cm$^{-1}$) can be expressed as

$$A = \int_{-\infty}^{+\infty} \alpha_v dv = PX_{abs} S(T)L$$

The combustion temperature can be obtained from the ratio of two line integrated absorbance area and the species concentration are acquired when $P$, $S(T)$, $L$ are known.
Tunable room-temperature quantum-cascade distributed-feedback lasers provide an access to stronger transitions of N$_2$O, CO and NO near 4.6 μm and 5.2 μm, respectively [14]. Since selected lines in mid-infrared bands are used for short optical path-length, multispecies simultaneous measurement, wavelength selection for each species is mainly considered by the line strength and isolation. Fig. 2 gives the line strengths of primary species in ADN monopropellant combustion over the range 1-6μm at a temperature of 1000 K. As noted in Fig. 2, strong transitions of N$_2$O and CO is partial overlapped near 4.6 μm, which is readily useful for simultaneous detection of N$_2$O and CO in a single period scan. Two N$_2$O transitions centered at 2192.48 and 2193.54 cm$^{-1}$ and one CO transition centered at 2193.36 cm$^{-1}$ near 4.6 μm are chosen to infer the mole fraction of multispecies. Meanwhile, NO transition centered at 1912.07 cm$^{-1}$ near 5.2 μm are selected to minimize interference of other combustion products in the combustion chamber, especially a large amount of water vapor. In addition, Two H$_2$O transitions at 7185.60 and 7444.35 cm$^{-1}$ are scanned respectively for temperature measurements, respectively. The two selected H$_2$O lines with well-known parameters have been applied to temperature measurements for variety of harsh combustion environments over temperature range of 400-2500 K reported in [15-17]. Spectroscopic parameters of all selected lines are presented in Table 1[13].

Table 1. Spectroscopic line parameters of N$_2$O,CO,NO,H$_2$O transitions used in the present study

| Species | Line-center Wavelength v$_0$ (cm$^{-1}$) | Line strength S(296K) (cm$^2$ atm$^{-1}$) | Lower state energy E'' (cm$^{-1}$) |
|---------|----------------------------------------|----------------------------------------|---------------------------------|
| N$_2$O  | 2192.48                                | 8.39                                   | 469.91                          |
|         | 2193.54                                | 9.30                                   | 442.28                          |
| CO      | 2193.36                                | 6.02                                   | 349.70                          |
| NO      | 1912.07                                | 2.64                                   | 200.63                          |
| H$_2$O  | 7185.597                               | 0.0197                                 | 1045.058                       |
|         | 7444.35+                               | 0.00112                                | 1774.751                       |
|         | 7444.37                                | 1806.670                               |                                 |
III. Experimental Setup

A. Thruster characterization and scheme for optical arrangement

Measurements were conducted on a 1-Newton ADN based thruster, as shown in Fig. 3. The experimental ADN thruster was composed of a solenoid valve, an injector, a catalyst bed, a combustion chamber and a nozzle. Sheathed heater was attached to the outer wall of catalyst bed for preheating. ADN liquid monopropellant was composed of 61% ADN, 27% water, and 12% methanol by mass. When the thruster operated, the liquid propellant was atomized into droplets by the injector, gasified and catalytically decomposed into gaseous intermediates by preheated catalyst particles in the catalytic bed, and finally reacted in the combustion chamber and discharged through the nozzle. The ADN based thruster was operated under two standard conditions: steady-state firing and pulse-mode firing. In the present experiments, steady-state firing was performed at duration of 10 s and pulse-mode firing was conducted at pulse duration of 100 ms to 2 s for 10 pulse trains operation. Hot firing tests were carried out over feed-pressure range of 5-12 bar at ignition temperature of 200 °C.

For optical measurements, two sapphire windows with 12.7mm in diameter were installed in the walls of the combustion chamber with 10x3.5mm² effective light area and the combustion chamber was manufactured with thicker wall for optical window implementation, as shown in Fig. 3. All windows were wedged with 3° on the outer face to avoid interference from internal etalon-type reflections as laser beams passed through.

B. Laser based absorption diagnostic system

Fig. 3 presents the arrangement of laser based absorption diagnostic system in this study. Optical measurements for the ADN based thruster confronted challenges due to its small-sized combustion chamber with optical path length of 14mm, requiring cautious optical layout. Two distributed-feedback (DFB) quantum cascade lasers (Alpes Lasers, Neuchatel, Switzerland) were used: one laser near 4.6 μm for N₂O, CO simultaneous measurements and another laser near 5.2 μm for NO measurement, respectively. Meanwhile, two DFB InGaAsP lasers (NEL NLK1B5EAAA) were used to monitor water vapor transitions in near-IR. Scanned-wavelength direct absorption is utilized to target the transitions, while wavelength modulation spectroscopy is not applicable here because of inaccurate broadening coefficients associating with such high pressures and complex components composition in the combustion chamber of ADN based thruster.

For concentration measurements, output of the quantum cascade laser was tuned by changing the temperature of the laser chip and injection current, which were modulated by Alpes Lasers TC-3 and ILX Lightwave LDX-3232, respectively, while a pump-driven water chiller was used to cool the laser device. The laser wavelength was scanned over the entire absorption feature of the target transitions by injection current using a sawtooth signal at a frequency of 100 Hz and constant tuning temperature. Collimated output of the laser was divided into two beams by a splitter. One beam was transmitted through the combustion chamber, focused by a lens, then passed through a filter and finally detected by a liquid nitrogen cooled InSb
detector (Infrared Associates, Inc.). The second beam was propagated through a silicon etalon (LightMachinery, Inc.) with a free spectral range (FSR) of 0.018 cm$^{-1}$ to provide calibration between the time and wavelength domains and detected by another InSb detector.

For temperature measurements, the diode laser temperature and current were modulated by a diode-laser controller (ITC4001, Thorlabs) and the laser wavelength was tuned using a ramp at a frequency of 1 kHz via a time division multiplexing (TDM) strategy. A 2 mm-diameter fiber-coupled collimator was used to ensure the multi lights passing through the optical path closely. The transmitted signals were collected by a multi-mode fiber and then detected by an InGaAs detector. The optics and detector were situated close to the window and were purged with nitrogen to remove any interfering absorption by ambient water vapor. Additional measurement of combustion pressure was carried out using a high frequency pressure sensor with response frequency of 20 kHz. All detector signals were acquired by oscilloscopes (DPO3034, Tektronix).

Laser based absorption measurements was path integrated in nature. Therefore, if the optical path exhibited non-uniformity in terms of temperature and/or concentration, the LAS measurements yielded average values for temperature and concentration. Previous study has been aimed at quantifying nonuniformity for path-averaged measurements [30]. In the case of the ADN based thruster employed in the present study, cross-section of the combustion chamber was quasi-uniform and combustion of the ADN monopropellant was assumed to be a quasi-one-dimensional flow along the axial direction [31].

IV. Results and Discussions

A. Measurements for Steady-state Firing

Measurements for steady-state hot firing was performed for 10 s duration at ignition temperature of 200 °C and over feed pressure range of 5-12 bar, in which the thruster standard operation corresponded to feed pressure of 12 bar. Measured position was installed at the center of the combustion chamber along the axis. The 4.6 μm quantum cascade laser was firstly used to measure N$_2$O and CO, then the 5.2 μm laser was exchanged for NO measurement while other devices remained unchanged, as shown in Fig.3. All experiments were conducted under the same operation condition in the same day. As shown in Fig.4, measurements of the combustion pressure were always conducted and the measured pressure trace showed great consistency in different runs under the same operation conditions, indicating the thruster operation were highly repeatable and allowing direct comparison between the two QCL sensors results. As the thruster firing initiated, the combustion pressure rapidly increased and reached equilibrium until the firing ended. The equilibrium steady-state value of the combustion pressure decreased and the corresponding equilibrium time increase with the feed pressure gradually decreased.

Fig. 4 Measured pressure in the combustion chamber for steady-state firing.

Fig.5 presents the measured concentration of N$_2$O, NO, CO for 10 s steady-state firing under the feed-pressure operation conditions. The concentration of N$_2$O and NO increased, indicating rapidly
decomposition of ADN synchronizing with the thruster operation. Then the N$_2$O and NO values decreased and reached equilibrium at levels close to zero. Meanwhile, the concentration of CO gradually increased as the methanol-related combustion went on, and partial CO was further oxidized to CO$_2$ and the CO values reached equilibrium at levels of 3-6%. As the detailed enlargement of the N$_2$O measurements showed, the increase and decrease of N$_2$O clearly identify the ADN decomposition and methanol-related combustion, respectively. The reaction rate of decomposition and combustion decreased as the feed pressure decreased from 12 bar to 5 bar, leading to slower heat release and lower combustion pressure corresponding to the results in Fig.4. Consistent evolution of the measured NO and CO was found as the thruster operated over the feed-pressure range.

![Graph](image)

**Fig. 5 Measured concentration of N$_2$O, NO, CO in the combustion chamber for steady-state firing.**

Results of the gas temperature in the combustion chamber for steady-state firing are shown in Fig.6(a). For the thruster standard operation, the combustion temperature rapidly increased and reached equilibrium with a value of nearly 1500 K. For comparison, the experimentally determined temperature for pure ADN combustion at 0.5 MPa was 1350 K [10] and the numerical result for the equilibrium temperature in the combustion chamber when operating an ADN monopropellant thruster was nearly 1600 K [18]. The thruster chamber wall temperature ranged from 1100 to 1480 °C during steady-state firing in the HPGP thruster developed by ECAPS [6].

As the feed pressure decreased, slower equilibrium of the combustion temperature was obtained, following with larger vibration. The results demonstrated transition from combustion stability to combustion instability for 10 s thruster operation and indicated worse performance of the thruster. Fig.6(b) gives the average value of combustion temperature during the 10s operation under different feed pressure. Over the feed pressure range of 9-12 bar, the average temperature kept at nearly 1450 K, indicating stable combustion for the thruster operation. Then the average temperature decrease sharply from 1400 K to 1150 K as the feed pressure further decreased below 8 bar, indicating unstable combustion for the thruster operation. It can be concluded that there existed pressure lower-limit threshold to ensure normal operation for the thruster steady-state firing.

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B. Measurements for Pulse-mode Firing

Measurements for pulse-mode firing were conducted for 10 pulse trains operation (100 ms ON and 2 s OFF). Fig. 7 gives the measured results of the combustion pressure under the feed-pressure operation conditions. The combustion pressure sharply increased as the pulse firing initiated and decreased as the pulse firing ended, showing good consistency with the pulse trains and indicating great performance for the thruster pulse-mode operation. As the pulse trains carried on, the maximum pressure values during one pulse operation gradually increased, which were lower than the corresponding values for steady-state firing. For the last pulse operation as shown in the enlargement of Fig. 7, the combustion pressure decreased as the feed pressure dropped.
Fig. 8 presents the measured concentration of N$_2$O, NO, CO for pulse-mode firing under the feed-pressure operation conditions. The concentration of N$_2$O, NO, CO generated rapidly as the pulse firing started, while the multispecies values slowly decreased as the firing ended for the first few pulses and was gradually in consistency with the pulse train operation, indicating increasing reactions degree and better performance for the thruster pulse-mode operation. For N$_2$O and NO measurements, the maximum values of each pulse decreased as the pulse trains carried on, further implying increasing combustion reactions. For 10 pulse trains firing, incomplete combustion was obtained as the maximum CO of each pulse varied over 2-8% as the pulse trains went on. For the last pulse train firing, both the increase and decrease rate of N$_2$O reduced as the feed pressure dropped, demonstrating slower degree of decomposition and combustion of the ADN monopropellant.
each pulse operation were irregularly varied under different feed-pressure operations. It should be note that the temperature vibration directed by the arrow in Fig.9 was not in coincidence with the real combustion situation which the combustion temperature should be stable. The reason is because unreacted gas-liquid phase products contaminated the sapphire window and interfered the optical measurement when laser beam was just passing through.

V. Conclusion

Simultaneous laser-based absorption measurements of N₂O, CO, NO and gas temperature were performed in a small-sized ammonium dinitramide (ADN) based thruster employing mid-IR quantum cascade lasers and near-IR diode lasers. In situ measurements were conducted in the center cross section of the combustion chamber under the feed-pressure operation conditions for both steady-state firing and pulse-mode firing. Time-resolved results provided quantitative information to gain insight into the combustion process inside the thruster and clarify the decomposition of ADN and methanol-related combustions. Measurements for steady-state firing showed that the measured the increase and decrease of N₂O represented the reaction rates of decomposition and combustion, which decreased as the feed pressure dropped corresponding to decreasing combustion pressure. Moreover, there existed pressure lower-limit threshold (>8 bar) for the thruster normal operation based on the temperature results. Measured results of multispecies concentrations and gas temperature for pulse-mode firing were in great consistency with the pulse trains. According to the N₂O measurements, increasing decomposition of ADN was found as the feed pressure raise and the combustion reaction rate gradually increased as pulse trains carried on, indicating incomplete equilibrium for 10 pulse trains operation. The laser-based absorption sensor demonstrated its capability for small-sized thruster applications and could be used as a normal combustion diagnostic technique for thruster hot firing tests.

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References

[1] Gohardani, A. S., Stanojev, J., Demaire, A., Anflo, K., Persson, M., Wingborg, N., and Nilsson, C. "Green space propulsion: Opportunities and prospects," Progress in Aerospace Sciences Vol. 71, 2014, pp. 128-149. doi: DOI 10.1016/j.paerosci.2014.08.001
[2] Larsson, A., and Wingborg, N. "Green Propellants Based on Ammonium Dinitramide (ADN)," Advances in Spacecraft Technologies, 2011, pp. 139-156.
[3] Anflo, K., Grö nland, T.-A., Bergman, G., Johansson, M., and Nedar, R. "Towards green propulsion for spacecraft with ADN-based monopropellants," 38 th AIAA Joint Propulsion Conference, AIAA Paper. Vol. 3847, 2002, p. 2002.
[4] Lange, M., Lein, A., Gotzig, U., Ziegler, T., Anthoine, S., Persson, M., and Anflo, K. "Introduction of a high-performance ADN based monopropellant thruster on the Myriade propulsion subsystem Technical and Operational Concept and Impacts," Proceedings of 6th International Conference on Recent Advances in Space Technologies (Rast 2013), 2013, pp. 549-553.
[5] Anflo, K., and Mollerberg, R. "Flight demonstration of new thruster and green propellant technology on the PRISMA satellite," Acta Astronautica Vol. 65, No. 9-10, 2009, pp. 1238-1249. doi: 10.1016/j.actaastro.2009.03.056
[6] Nils, P., Kjell, A., and Oskar, S. "Spacecraft System Level Design with Regards to Incorporation of a New Green Propulsion System," 47th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit. American Institute of Aeronautics and Astronautics, 2011.
[7] Anflo, K., and Crowe, B. "In-Space Demonstration of an ADN-based Propulsion System," 47th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit. American Institute of Aeronautics and Astronautics, 2011.
[8] Vyazovkin, S., and Wight, C. A. "Ammonium dinitramide: kinetics and mechanism of thermal decomposition," The Journal of Physical Chemistry A Vol. 101, No. 31, 1997, pp. 5653-5658.
[9] Bottaro, J. C., Penwell, P. E., and Schmitt, R. J. "1, 1, 3, 3-Tetraoxo-1, 2, 3-triazapropene anion, a new oxy anion of nitrogen: the dinitramide anion and its salts," Journal of the American Chemical Society Vol. 119, No. 40, 1997, pp. 9405-9410.
[10] Sinditskii, V. P., Egorshev, V. Y., Levshenkov, A. I., and Serushkin, V. "Combustion of Ammonium Dinitramide, Part 2: Combustion Mechanism," Journal of Propulsion and Power Vol. 22, No. 4, 2006, pp. 777-785. doi: 10.2514/1.17955

American Institute of Aeronautics and Astronautics
[11] Korobeinichev, O. P., Bolshova, T. A., and Paletsky, A. A. "Modeling the chemical reactions of ammonium dinitramide (ADN) in a flame," Combustion and flame Vol. 126, No. 1, 2001, pp. 1516-1523.
[12] Zeng, H., Li, F., Zhang, S., Yu, X., Zhang, W., and Yao, Z. "Midinfrared Absorption Measurements of Nitrous Oxide in Ammonium Dinitramide Monopropellant Thruster," Journal of Propulsion and Power, 2015, pp. 1-5. doi: 10.2514/1.B35648
[13] Rothman, L., Gordon, I., Babikov, Y., Barbe, A., Benner, D. C., Bernath, P., Birk, M., Bizzocchi, L., Boudon, V., and Brown, L. "The HITRAN2012 molecular spectroscopic database," Journal of Quantitative Spectroscopy and Radiative Transfer Vol. 130, 2013, pp. 4-50.
[14] Namjou, K., Cai, S., Whittaker, E., Faist, J., Gmachl, C., Capasso, F., Sivco, D., and Cho, A. "Sensitive absorption spectroscopy with a room-temperature distributed-feedback quantum-cascade laser," Optics letters Vol. 23, No. 3, 1998, pp. 219-221.
[15] Li, F., Yu, X. L., Gu, H. B., Li, Z., Zhao, Y., Ma, L., Chen, L. H., and Chang, X. Y. "Simultaneous measurements of multiple flow parameters for scramjet characterization using tunable diode-laser sensors," Applied Optics Vol. 50, No. 36, 2011, pp. 6697-6707. doi: Doi 10.1364/Ao.50.006697
[16] Liu, J. T., Rieker, G. B., Jeffries, J. B., Gruber, M. R., Carter, C. D., Mathur, T., and Hanson, R. K. "Near-infrared diode laser absorption diagnostic for temperature and water vapor in a scramjet combustor," Applied Optics Vol. 44, No. 31, 2005, pp. 6701-6711.
[17] Sanders, S. T., Baldwin, J. A., Jenkins, T. P., Baer, D. S., and Hanson, R. K. "Diode-laser sensor for monitoring multiple combustion parameters in pulse detonation engines," Proceedings of the Combustion Institute Vol. 28, No. 1, 2000, pp. 587-594.
[18] Zhang, T., Li, G. X., Yu, Y. S., Sun, Z. Y., Wang, M., and Chen, J. "Numerical simulation of ammonium dinitramide (ADN)-based non-toxic aerospace propellant decomposition and combustion in a monopropellant thruster," Energy Conversion and Management Vol. 87, 2014, pp. 965-974. doi: DOI 10.1016/j.enconman.2014.07.074