REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*

2. REPORT TYPE
Technical Papers

3. DATES COVERED *(From - To)*

4. TITLE AND SUBTITLE
Please see attached

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

5d. PROJECT NUMBER
1011

5e. TASK NUMBER
00 46

5f. WORK UNIT NUMBER
346204

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/PRS
5 Pollux Drive
Edwards AFB CA 93524-7048

8. PERFORMING ORGANIZATION REPORT

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
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10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S NUMBER(S)
Please see attached

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

20030116 047

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Leilani Richardson
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified	A		19b. TELEPHONE NUMBER *(include area code)* (661) 275-5015

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. 239.18

MEMORANDUM FOR PR (In-House Publication)

FROM: PROI (TI) (STINFO) 05 Jun 2000

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-2000-123**
Harper, J., "Progress in Advanced Propellant Research"

NASA JPL-MSFC 11th Advances Space Propulsion Research Workshop (Statement A)
(Pasadena, CA, 31 May-02 Jun 00) (Submission Deadline: 02 Jun 00)

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ROBERT C. CORLEY (Date)
Senior Scientist (Propulsion)
Propulsion Directorate

Progress in Advanced Propellant Research

- **Cryogenic HEDM Solids**
- **Polynitrogen Compounds**
- **High Performance Monopropellants**
- **Hydrocarbon Fuels**

Capt. Jessica Harper
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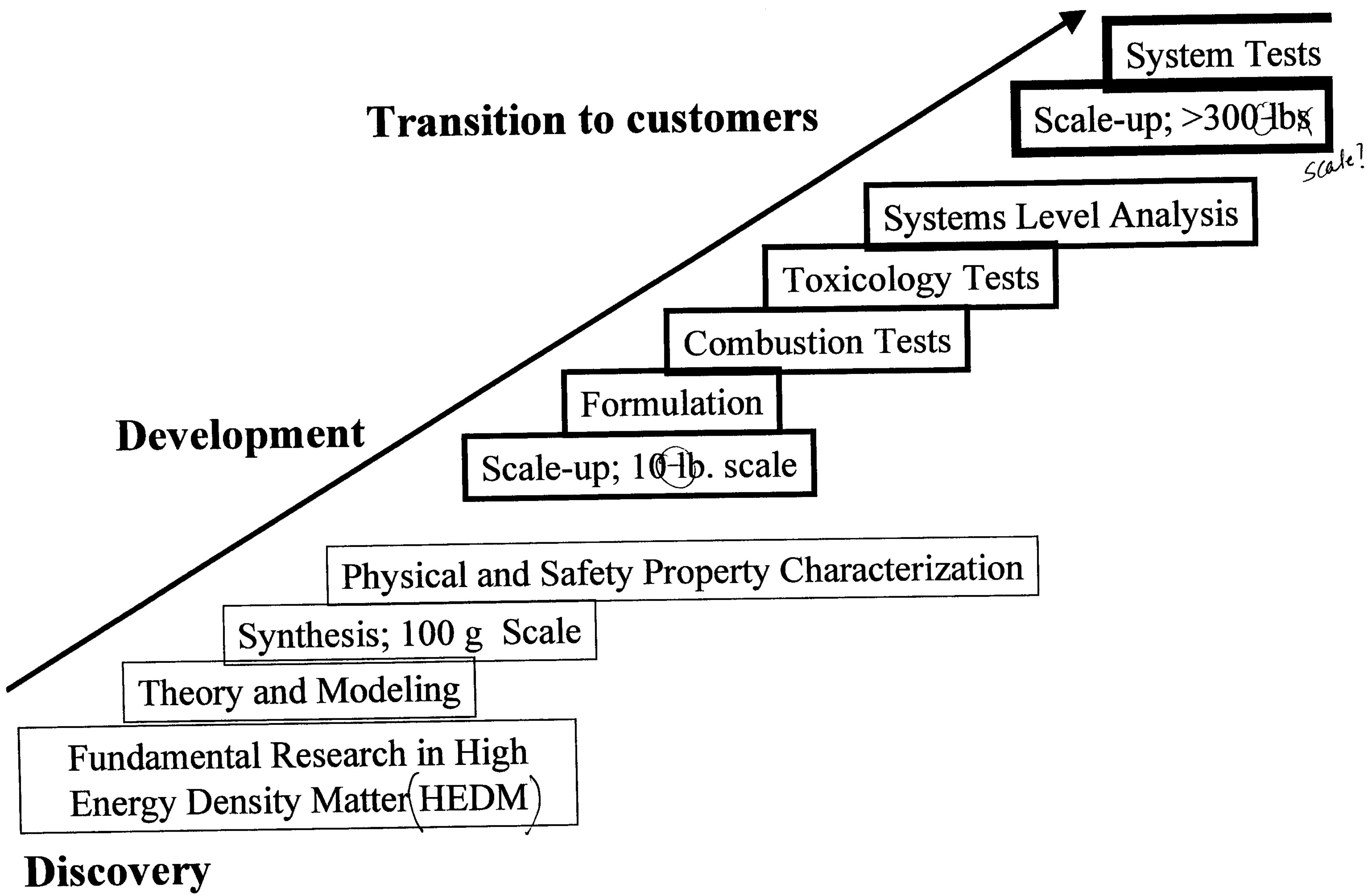
Propulsion Directorate mission includes discovery and development of envolutionary and revolutionary advances in propulsion systems

Distribution A: Unlimited Release
(I have added this to my cover slide. JH)

Technology Development Path



Cryogenic Solid HEDM Propellants

Use a solidified fuel or oxidizer as a storage medium for energetic additives, obtaining density and specific-impulse improvements

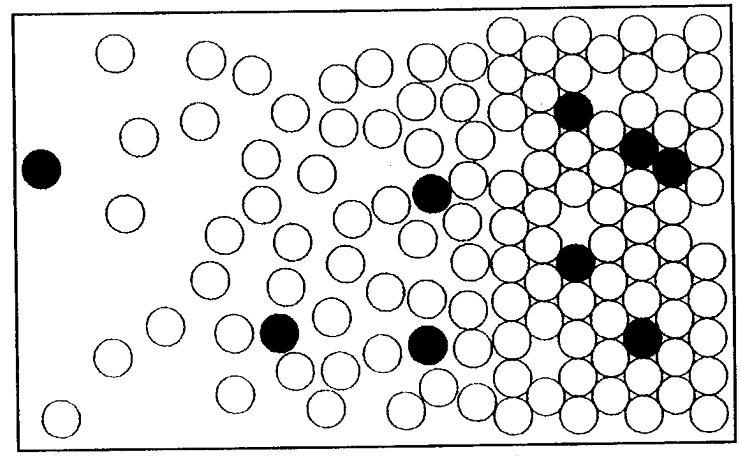
Depositing certain atomic or molecular species in solid hydrogen at 5% concentrations can increase specific impulse by more than 20%

Vehicle	Propellant	Payload Mass (lb)	Payload (lb) With 10% Density Increase	Payload (lb) With 10% Isp Increase	Payload (lb) With 10% Increase in Both
Rockwell SSTO RLV	LH2/LOX (Isp = 455 s)	40,000	51,200 **(+28%)**	68,000 **(+70%)**	76,800 **(+92%)**

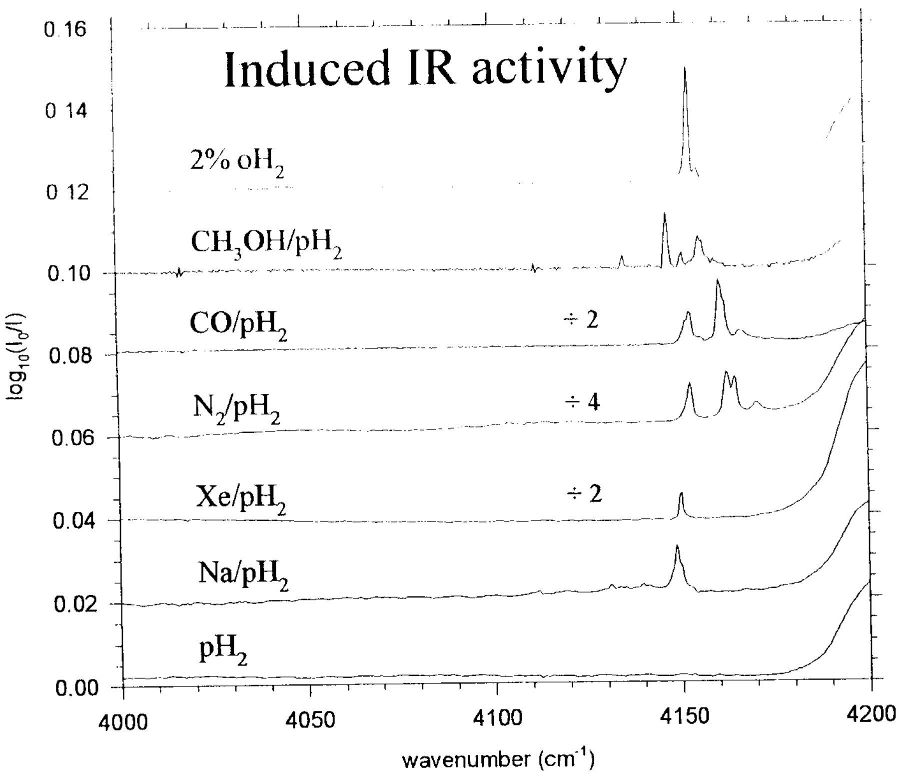
Large payload increases are achievable with modest density or specific impulse increases

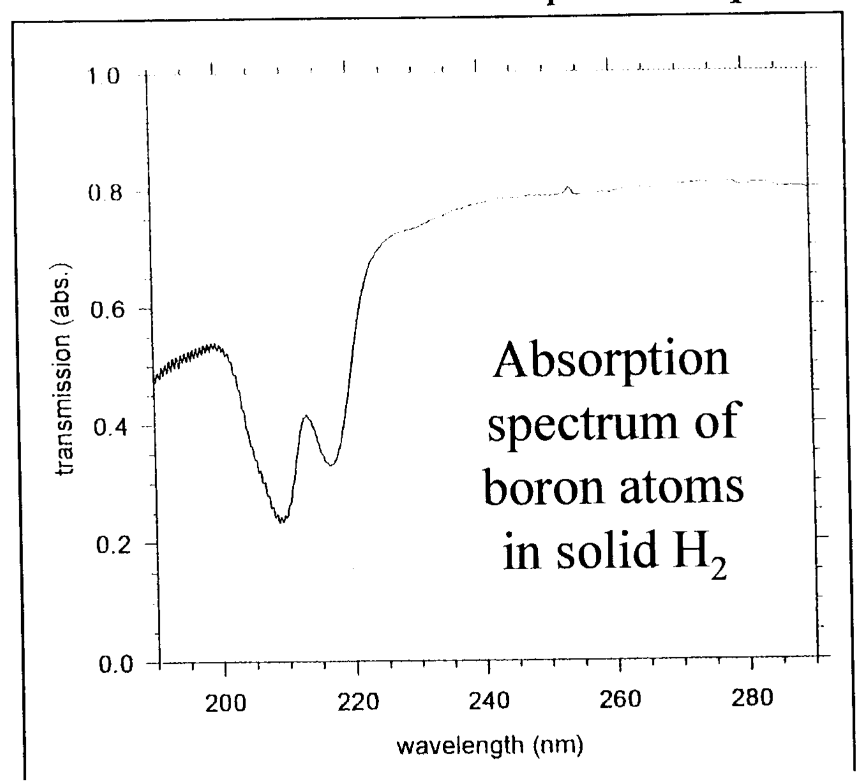
Cryogenic Solid HEDM Propellants

- ***KEY ISSUE*** Develop methods to characterize thick cryogenic solids with high additive concentrations
- ***APPROACH*** Investigate how direct dopant absorptions and the dopant-induced IR activity of H_2 relate to the type and concentration of HEDM additives.



Schematic of the deposition process





Cryogenic Solid HEDM Prospectus

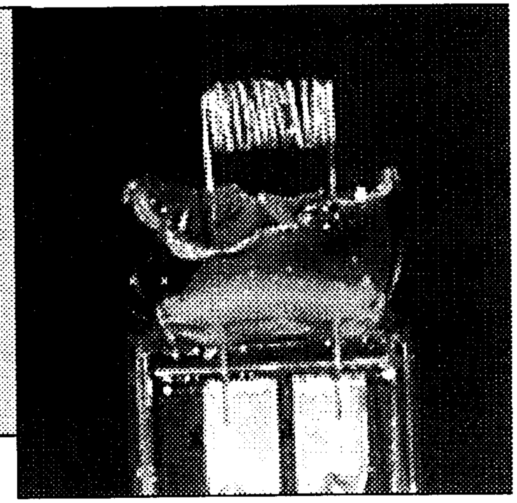
BASELINE	Isp (sec)
Solid H2	389
5% ADDITIVE	
H	407
Be	452
B	472
C	469
Al	425
BH	449
CH	433
LiB	494
LiC	465
B2	492
BC2	482
B2C2	439

•*KEY ISSUE* Develop and characterize high-flux, robust, pure sources of desirable HEDM additives

•*APPROACHS*

Boron filament source

Commercial aluminum deposition source

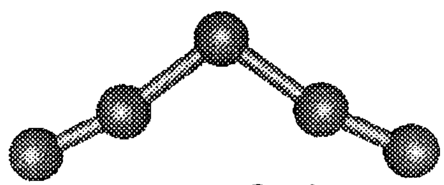


•*KEY ISSUE* Determine reactivity, diffusion, and recombination propensities to identify the most stable additives

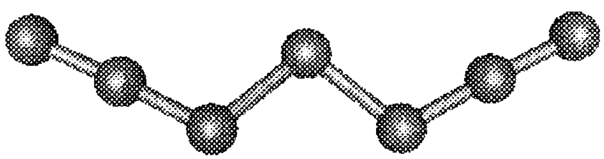
•APPROACH Simulations and experiments are yielding significant information about the chemical and thermal stabilities of doped solid H_2 and the dopant concentration limits.

Polynitrogen Calculations Led to Synthesis

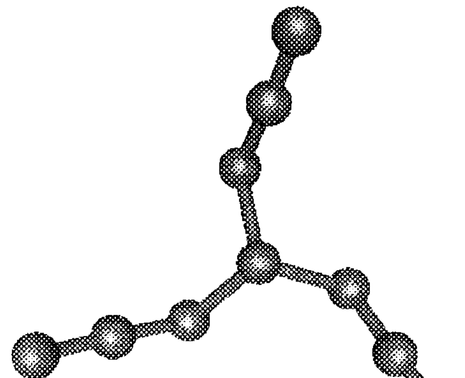
Program Objective: Synthesize and characterize new highly energetic polynitrogen compounds



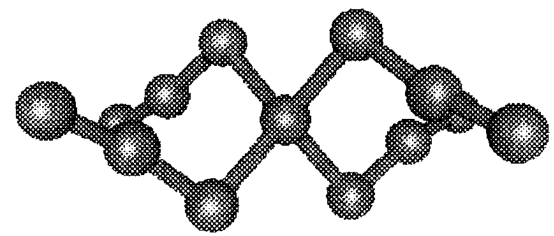
N_5^+ (C_{2v})



$N(N_3)_2^-$ (C_2)



$N(N_3)_3$ (C_3)

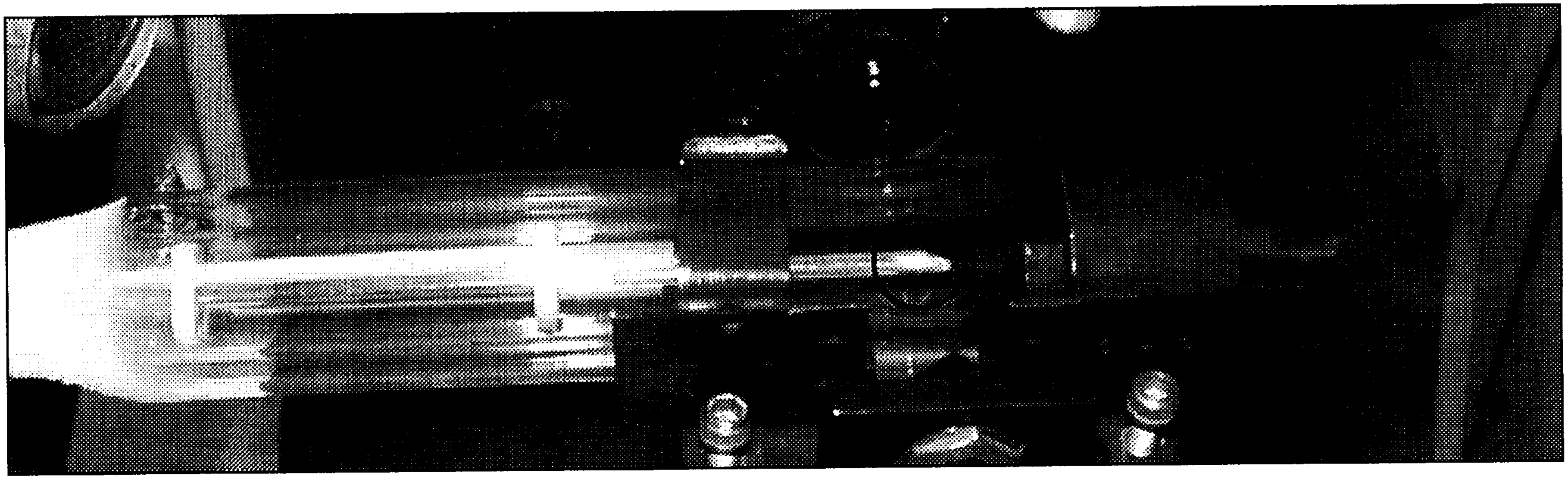


$N(N_3)_4^+$ (D_{2d})

- Calculations showed that the compounds depicted above are all stable, albeit to varying extents, and highly energetic
- Predicted measurable properties to help chemists identify what they made

This project is co-funded by DARPA and AFOSR

N_5^+ Salt in Low-Temperature Raman Spectrometer: Before and After Explosion



All Nitrogen Compound

Program Goal: Discover, characterize, and scale-up production of highly energetic all-nitrogen compounds for use as propellants or explosives.

Drs. Karl Christe, William Wilson, Jeffrey Sheehy, Jerry Boatz

Recent Accomplishments

- The N_5^+ cation is the first all-nitrogen compound to be prepared in bulk in over 100 years, and it is only the third known compound of this type
- Improved synthesis yields 5 g of N_5^+ salt in high purity at a fraction of the time of the previous synthesis
- A remarkably stable $N_5^+SbF_6^-$ salt was unambiguously identified by vibrational and NMR spectroscopy of unlabeled and ^{15}N-labeled N_5^+ in conjunction with quantum-chemical calculations
- Based on this initial success, the synthesis of additional new polynitrogen compounds is planned. A particular target is N_8, which could be formed as the ionic salt $N_5^+N_3^-$, or as a covalent compound such as azidopentazole

Significance

- Named one of "Chemistry's Top Five Achievements in 1999" by the American Chemical Society
- The feasibility of polynitrogen-based HEDM compounds has been demonstrated by the successful bulk synthesis of N_5^+
- Demonstrates synergy of calculations and experiment. Modeling and simulation were used to predict that the compound should exist, and computed spectra made it possible to identify and characterize the new N_5^+ compound
- Stable, neutral polynitrogens would be high performance monopropellants or explosives. N_8 as a monopropellant would have an Isp of 420 s, compared with hydrazine at 233 s. Clean propellant would have cost savings in handling, production, logistics, and disposal.

Monopropellant Development

Objective:
1) Develop monopropellants with higher performance and lower toxicity than SOTA (hydrazine). 2) Develop monopropellant to exceed bipropellant performance

Approach:
1) Synthesize and characterize energetic liquid salt ingredients

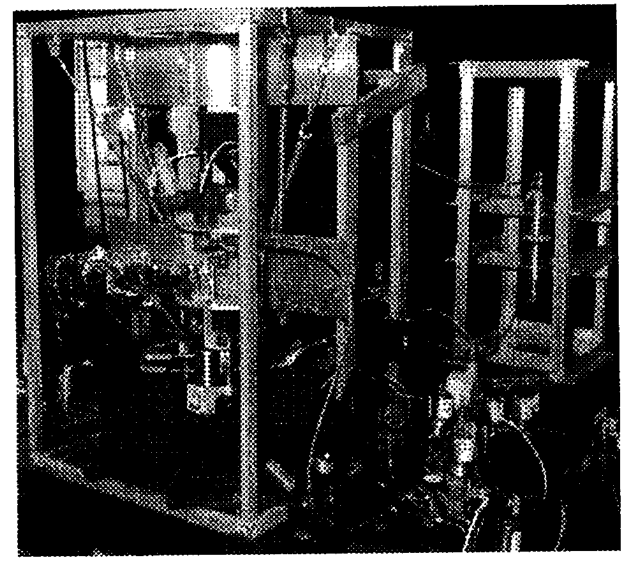
2) Formulate monopropellants with new ingredient

3) Combustion testing of formulations

Motives:
1) Enable AF satellite missions; AF aerospace vehicle; reduced size boost vehicle

2) Enable NASA small (< 100 kg) spacecraft and SSTO vehicles

3) Meet IHPRPT Phase II and III goals



Monopropellant Thrust Stand

(Economics of Space Transportation study (NASA-HQ) shows high energy density monoprops shrink vehicle size and cost for "generation-after-next" SSTO vehicles.)

High Performance, Reduced Toxicity Monopropellants

Properties	RK-618A	RK-315E	RK-100A	Hydrazine
Density Isp, % over SOTA (a)	+58	+61	+24	0.0
Chamber Temp. (Theoretical), K	2070	2083	1369	883
Carbon Content of Exhaust; (b)	none	none	none	none
Impact Sensitivity*, kg-cm (5 negatives)	>200	60	>200	>200
Friction Sensitivity, N (5 negatives)	318	300	>371	>371
NOL Card Gap (at 69 Cards)	negative	negative	negative	negative
Thermal Stability, %wt loss/48hr, 75°C	< 0.5	1.96	10.2	(< 0.1)
Melt Point, °C	5 (c)	<-22	-39	1

a: Theoretical, calculated with 300 psi chamber pressure, exhaust to vacuum, 50/1 expansion
b: as soot or solid carbon (by theoretical computation)
c: by DSC; melt transition was broad, melt peak reported
*: For reference, n-propylnitrate had an impact sensitivity of 8 kg-cm

RK-618 and RK-315 Propellants Display Acceptable Safety/Sensitivity Properties For Continued Development

Advanced Monopropellants

Dr. Tom Hawkins, Dr. Greg Drake, Adam Brand,
Milton McKay, Dr. Ismail Ismail

Recent Accomplishments	Significance
• Thruster test of low-toxicity monopropellant at National Hover Test Facility at PR-w and at Atlantic Research Corporation. Determined catalyst behavior, and C*, exhaust products.	• Technology transfer and evaluation in commercial industry of monopropellant with theoretical density impulse increase of 61% over hydrazine. Verifies in-house thruster test results.
• Synthesized and tested a dozen new ingredients. Identified a compound for scale-up.	• Theoretical monopropellant performance with new ingredients equals or exceeds current bipropellant (NTO/MMH) systems.
• Toxicology assessment, completed by AFRL/HE (Dr. Dave Mattie), shows these monoprops 6X less oral toxicity than hydrazine. Very low dermal irritation.	• Verifies that these propellants will have cost savings in handling, production, logistics, and disposal. Environmentally benign as well.
• Gelled monopropellant developed.	• Increases range of operability for some systems.
• Numerous collaborators--Primex, ARC, NASA/GRC, small businesses...	• Sharing resources will advance the program at a faster rate.

Liquid Hydrocarbon Fuels

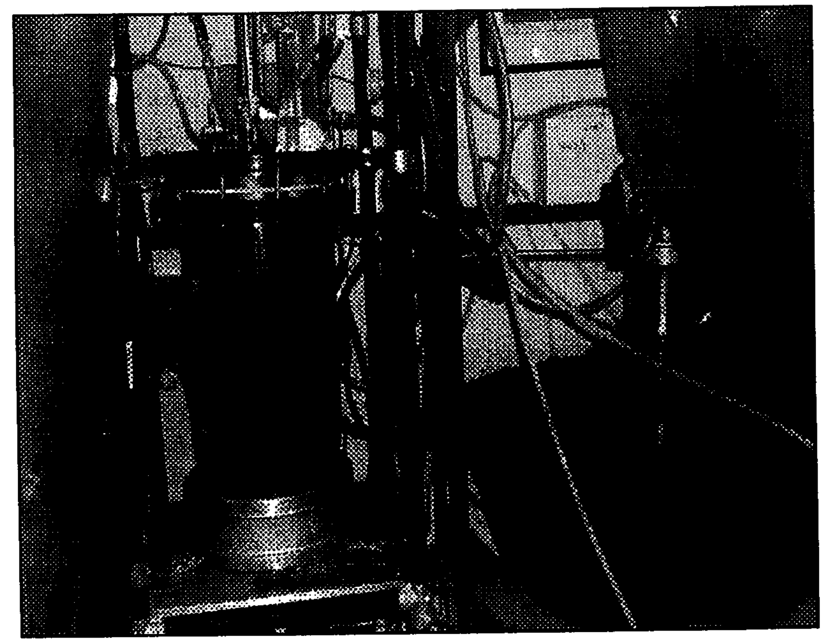
Objective:
Develop cost-effective high energy, high density liquid hydrocarbons to enhance or replace RP and JP fuels.

Approach:
1) HEDM synthesis; novel molecules; property testing
2) 10 lb. scale-up of promising candidates; combustion testing
3) Scale up to ton quantities through business collaborations

Motives:
1) Enable new AF missions (air breathers or rockets)

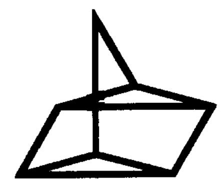
2) NASA Access to Space concepts--supported with $200K in FY99; $50K likely in FY00

3) Meet IHPRPT Phase II and III goals



30L scale-up equipment at AFRL

Theoretical Performance Comparison of Energetic Hydrocarbons



Hydrocarbons	H/C ratio	Density g/ml	Calc.ΔHf (Kcal/mole)	Calc.Isp sec
RP-1	1.9	0.80	-	300.0
Quad	1.14	0.98	72.2	307.0
BCP	1.33	0.85	76.1	312.5
AFRL-1	1.2	0.77	64.0	311.3
AFRL-2	1.25	0.87	73.4	307.2
AFRL-3	1.0	0.93	123.6	307.2
AFRL-4	1.0	-	129.6	321.4

Energetic Hydrocarbon Fuels

Dr. Suresh Suri, Mike Tinnirello, Paul Jones

Recent Accomplishments

- Four energetic hydrocarbons (BCP, AFRL-1, quadricyclane, 1,7 octadiyne) passed physical property, material compatibility, and thermal stability tests.
- Improved bicyclopropylidene (BCP) bench-scale synthesis to produce ~8 lbs.
- Delivered three energetic hydrocarbons (BCP, quadricyclane, 1,7 octadiyne) to NASA/MSFC for combustion testing.
- Initial tests by AFRL/HE determined quad and BCP to have low toxicity.
- BCP shown to be hypergolic with N2O4, IRFNA and possibly H2O2.
- Synthesized AFRL-3.

Significance

- Candidates have passed initial hurdles. All are suitable for combustion testing.
- First time BCP produced in these quantities. Material now available for testing.
- Combustion results will indicate candidates potential for further scale-up.
- Verifies that these propellants can be handled in the same way as RP-1.
- BCP could be lower toxicity replacement for MMH. May enable new design of systems that burn nonhypergolic propellants.

Summary

- Cryogenic solid HEDM doped with energetic atoms and molecules is being pursued with special attention on how to produce and measure 5% dopants in solid H_2.

- Synthesis of the N_5 cation was a breakthrough towards making a high energy all nitrogen propellant.

- Low toxicity high performance monopropellants offer dramatic improvements over hydrazine.

- Fruitful collaboration with NASA/MSFC; will test fire BCP, 1,7-octadiyne, quadricyclane in 100-lb. thruster; Hydrocarbon program has products close to transition.