Please see attached

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Unclassified

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Unclassified Unclassified Unclassified
MEMORANDUM FOR PRS (In-House Publication)

FROM: PROI (STINFO) 22 March 2002

Jeff Sheehy, et al. (PRSP), “Computational Chemistry Studies of HEDM”

AF Chief Scientists
(Edwards AFB, CA, 07 March 2002) (Deadline: Past Due)  (Statement A)

1. This request has been reviewed by the Foreign Disclosure Office for: a.) appropriateness of distribution statement, b.) military/national critical technology, c.) export controls or distribution restrictions, d.) appropriateness for release to a foreign nation, and e.) technical sensitivity and/or economic sensitivity.
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Comments: ____________________________________________________________
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_____________________________________________________________________

APPROVED/APPROVED AS AMENDED/DISAPPROVED

PHILIP A. KESSEL Date
Technical Advisor
Space and Missile Propulsion Division
High Energy Density Materials (HEDM) Program Objective

Identify and develop advanced chemical propellants for rocket propulsion applications

- Hydrocarbons for liquid boosters
- Liquid & solid oxidizers for boost and upper stages
- Monopropellants for upper stages and satellites
- Cryogenic propellants for upper stages

Breaking the performance barrier
# HEDM Propellant Payoffs

"The highest leverage technology area impacting launch vehicles is the development of high-energy-density materials for use as propellants."
-- New World Vistas Panel on Space Technology (1995)

<table>
<thead>
<tr>
<th>Vehicle Type</th>
<th>Baseline Vehicle</th>
<th>Propellant</th>
<th>Takeoff Mass (lb)</th>
<th>Payload Mass (lb)</th>
<th>Payload Mass (lb) With 10% Isp Increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two-stage ELV</td>
<td>Atlas II // Centaur D-1A</td>
<td>RP-1/LOX (Isp = 295 s) // LH2/LOX (Isp = 455 s)</td>
<td>360,000</td>
<td>12,500</td>
<td>15,600 (+25%)</td>
</tr>
<tr>
<td>SSTO RLV</td>
<td>Lockheed SSTO</td>
<td>LH2/LOX (Isp = 455 s)</td>
<td>1,900,000</td>
<td>40,000</td>
<td>68,000 (+70%)</td>
</tr>
<tr>
<td>Missile Defense Interceptor</td>
<td>Boost-Phase Interceptor</td>
<td>HTPB/Al/HMX (Isp = 270 s)</td>
<td>1,847</td>
<td>74</td>
<td>110 (+49%)</td>
</tr>
</tbody>
</table>

*Our research is aimed at increasing propellant Isp by 5 to 50%*
HEDM Program General Approach

Employ a synergic blend of experimental, theoretical, and computational techniques derived from the disciplines of chemistry and physics.

- **Experiments**
  - Identify target compounds
  - Calculate stability and performance

- **Theory & modeling**
  - Exploreoretical experiments

- **Optimize synthesis methods**

- **Measure properties & compare with predictions**

- **Develop new synthesis methods**

- **Attempt synthesis on small scale**

- **Characterize new materials**

- **Model spectral fingerprints**

- **Scale up for formulation and testing**

- **Transition to Industry**
The Calculation of Molecular Properties

Various computational techniques are employed to solve the molecular electronic Schrödinger equation from quantum mechanics:

$$\left[-\frac{1}{2}\sum_i \nabla_i^2 - \sum_i \sum_{\alpha} \frac{Z_{\alpha}}{r_i \alpha} + \sum_i \sum_{j>i} \frac{1}{r_{ij}}\right] \Psi_{el} = E_{el} \Psi_{el}$$

**Determining what to synthesize:**
Thermodynamic properties relate directly to propellant performance and are obtained from relative energies of reactants, intermediates, and products.

**Determining how to synthesize them:**
Potential-energy surfaces – energy profiles associated with all degrees of freedom in a chemical system – give insight into stabilities and reaction & decomposition pathways.

**Determining whether we’ve made what we wanted to make:**
Structures and spectra (IR, Raman, NMR) are obtained by evaluating derivatives of the energy or other properties with respect to nuclear coordinates or applied fields.
DARPA Polynitrogen Program

Program began late FY98
Six groups funded to discover, scale up, and demonstrate polynitrogen propellants or explosives

AFRL / Edwards

Naval Research Laboratory

Los Alamos National Laboratory

Lawrence Livermore National Laboratory

Colorado School of Mines / National Renewable Energy Laboratory

Defense Research Establishment, Sweden

Only the AFRL group has been successful
Identifying a Completely New Molecule: Comparison of Calculated and Measured Spectra

\[
\left[^{15}\text{N}-^{14}\text{N}-^{14}\text{N}-^{14}\text{N}-^{14}\text{N}\right]^+\text{AsF}_6^- \quad \text{and} \quad \left[^{14}\text{N}-^{14}\text{N}-^{15}\text{N}-^{14}\text{N}-^{14}\text{N}\right]^+\text{AsF}_6^- 
\]

\text{\textbf{\textit{14N - 15N Isotopic Shifts (cm}^{-1})}}

<table>
<thead>
<tr>
<th>Mode</th>
<th>Obs.</th>
<th>Calc.†</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v_1(a_1))</td>
<td>12</td>
<td>11.8</td>
</tr>
<tr>
<td>(v_7(b_2))</td>
<td>21</td>
<td>21.4</td>
</tr>
<tr>
<td>(v_2(a_1))</td>
<td>14</td>
<td>14.1</td>
</tr>
</tbody>
</table>

†CCSD(T)/6-311+G(2d) results
This ion has been suggested as a useful precursor to new polynitrogen molecules...  ...but calculations predict it to be unstable.
Computational chemistry plays a critical role in HEDM research
Guides the choice of target compounds and possible synthetic routes, provides verification of successful synthesis.

CC is addressing an ever wider range of Air Force applications
New methods are under development (e.g., modeling chemistry in solution or on surfaces). Parallel computing technology has greatly expanded the scope of problems which can be modeled.

Access to high performance computing resources is essential
Many quantum chemical calculations are too costly and complex to perform on “standard” platforms (e.g., standalone workstations or desktop Linux PCs).