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MEMORANDUM FOR PRS (In-House Publication)

FROM: PROI (STINFO) 11 May 2001

Mario Fajardo and Michelle DeRose, “Status of Cryosolid Propellants Task”

AFOSR Molecular Dynamics Contractors' Meeting
(Irvine, CA, 21 May 01)  (Deadline: 18 May 01)

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PHILIP A. KESSEL Date
Technical Advisor
Space and Missile Propulsion Division
Status of CryoSolid Propellants Task

Mario E. Fajardo and Michelle E. DeRose

* Cryosolid Propellants Team
* HEDM Cryosolid Propellants Concept (Atoms in Solid Hydrogen)
* Cryosolid Propellants Payoffs, Objectives, Approach
* Requirement for Spectroscopic Diagnostics
* Rapid Vapor Deposition of Thick Parahydrogen (pH$_2$) Solids
* Update on Al/pH$_2$ and Mg/pH$_2$ Experiments
* Opportunities for Supporting In-House Effort
* Recommendations for Future Experiments
* Open Discussion
Cryosolid Propellants Team

* Mario E. Fajardo, Michelle E. DeRose, and Simon Tam
  Bill Larson and Jessica Harper (B atom source)

* J. Boatz, J. Mills, P. Langhoff, and J. Sheehy (in-house theory)

* FY00 Interactions with AFOSR Contractors:
  P. Dagdigen @ Johns Hopkins: Al/H₂ & B/H₂ Complexes
  M. Alexander @ U. Maryland: B/H₂ Interaction Potentials
  G. Voth @ U. Utah: Path-Integral Monte Carlo Simulations
  G. Scoles & K. Lehmann @ Princeton U.: Helium Clusters

* External Collaborators:
  T. Momose @ Kyoto U.: High Resolution IR Spectroscopy

* Summer Visiting Professors:
  R.J. Hinde @ U. Tennessee: Dopant-Induced IR Activity
  D. Anderson @ U. Wyoming: Dopant IR Absorptions
“Revolutionary” vs. “Evolutionary”
HEDM Concepts

* “Revolutionary” means better than LOX/LH$_2$:
  LOX/LH$_2$ \( \Delta H_{sp} = 12.6 \text{ MJ/kg (3.0 kcal/g)} \)
  HEDM Target: \( \Delta H_{sp} > 15.0 \text{ MJ/kg (3.6 kcal/g)} \)

* Early (c1990) Revolutionary HEDM Concepts:
  tetrahydrogen (H$_4$)
  metastable triplet helium (He* and He$_2^*$)
  spin-polarized atomic hydrogen (H$\uparrow$)
  high-spin species ($^5$CO)
  dications (AB$^{++}$, ABC$^{++}$)
  “non-metallics” (e.g. O$_4$/H$_2$, N$_4$, N$_8$, N$_{20}$)
  metallic hydrogen
  metal atoms and clusters in solid H$_2$
Cryosolid Propellants Concept

Use cryogenic solid hydrogen as a “packaging material” to store energetic species such as metal atoms and clusters.

\[ \Delta H_{sp} (\text{kcal/g}) = -3.2 \]

\[ \Delta H_{sp} (\text{kcal/g}) = -3.9 \]

\[ \alpha \text{Al}_2\text{O}_3 \]

\[ -4.7 \]
Cryosolid Propellants Payoffs

Increased Specific Impulse

\[ I_{sp} \propto \sqrt{\Delta H_{sp}} \]

- LOX/LH\textsubscript{2} : \( I_{sp} = 400 \text{ s} \)
- 5\% B/sh\textsubscript{2} + LOX : \( I_{sp} = 500 \text{ s} \) (+25\%)*
- 5\% Al/sh\textsubscript{2} + LOX: \( I_{sp} = 450 \text{ s} \) (+12\%)*

* calculated for \( P_{\text{chamber}} = 1000 \text{ PSIA} \), \( P_{\text{exhaust}} = 14.7 \text{ PSIA} \)

Greater Propellant Density

- liquid \( \text{H}_2 \) @ 20 K : \( \rho = 0.070 \text{ g/cm}^3 \)
- solid \( \text{H}_2 \) @ 2 K : \( \rho = 0.087 \text{ g/cm}^3 \) (+25\%)
- 50/50 liquid He/solid \( \text{H}_2 \) : \( \rho = 0.105 \text{ g/cm}^3 \) (+50\%)
Atom Additive Payoffs (5 % molar)

Sea level specific impulse, $I_{sp}$, in seconds (% change)

$P_{chamber} = 1000$ PSIA, $P_{exhaust} = 14.7$ PSIA

<table>
<thead>
<tr>
<th>Additive</th>
<th>in standard state</th>
<th>as atoms</th>
<th>monoprop.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M(5%)$/LOX/H$_2$</td>
<td>$M(5%)$/LOX/H$_2$</td>
<td>$M(5%)$/H$_2$</td>
</tr>
<tr>
<td>none</td>
<td>403</td>
<td>515 (+28%)</td>
<td>515 (+28%)</td>
</tr>
<tr>
<td>C</td>
<td>381 (-5%)</td>
<td>515 (+28%)</td>
<td>515 (+28%)</td>
</tr>
<tr>
<td>B</td>
<td>407 (+1%)</td>
<td>508 (+26%)</td>
<td>465 (+15%)</td>
</tr>
<tr>
<td>Be</td>
<td>427 (+6%)</td>
<td>493 (+22%)</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>400 (-1%)</td>
<td>460 (+14%)</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>407 (+1%)</td>
<td>454 (+13%)</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>403</td>
<td>430 (+7%)</td>
<td>380 (-6%)</td>
</tr>
<tr>
<td>Li</td>
<td>404</td>
<td>428 (+6%)</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>400 (-1%)</td>
<td>416 (+3%)</td>
<td></td>
</tr>
</tbody>
</table>
Cryosolid Propellants Objectives

* Make solid hydrogen samples (any size) containing 5% molar concentration of trapped energetic additives.

* Measure absolute concentrations of energetic species.

* Scale-up samples; produce ~ 1 cm$^3$ samples in our lab.

Example: 5% Al/pH$_2$, V = 1 cm$^3$
assume each Al atom replaces one H$_2$ molecule
$\Rightarrow$ 58 mg Al / 83 mg H$_2$ (*see display item*)
$\therefore$ $\rho = 0.142$ g/cm$^3$ (+100%)
Cryosolid Propellants Approach

* Rapid vapor deposition of metal atom vapor and pre-cooled parahydrogen gas onto a liquid helium cooled substrate in vacuum.
Recombination at High Concentrations

Bernoulli Trails (statistical) model of dopant agglomeration:  \[ P(k,12) = \binom{12}{k} f^k (1-f)^{12-k} \]
Requirement for Spectroscopic Diagnostics

* Develop spectroscopic techniques to identify and measure concentrations of trapped species.

* Beer’s Law: \[ A = \sigma N d \]
  
  \[ A = \text{absorbance} = -\ln \left( \frac{I}{I_0} \right) \]
  
  \[ \sigma = \text{absorption cross-section} \]
  
  \[ N = \text{species number densities} \]
  
  \[ d = \text{pathlength} \]
  
  \[ N \ d = \text{“column density”} \]

* UV/vis absorption for low metal atom column densities.

* IR absorptions, direct and dopant-induced pH\(_2\) transitions, for reaction products & metal atoms at large column densities.
The Perils of Calorimetry

TABLE IX
Concentrations of Free Radicals Reported

<table>
<thead>
<tr>
<th>Radical</th>
<th>Matrix</th>
<th>Mole per cent radicals</th>
<th>Method of production and estimate</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>O₂</td>
<td>4-20</td>
<td>Gas, cal</td>
<td>Minkoff et al. (1959)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&lt;3</td>
<td>Gas, IR</td>
<td>Harvey and Bass (1958)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>~1</td>
<td>Gas, cal</td>
<td>Broida and Lutes (1956)</td>
</tr>
<tr>
<td>OH</td>
<td>Ca(OH)₂</td>
<td>0.6</td>
<td>γ, ESR</td>
<td>R. Livingstonb</td>
</tr>
<tr>
<td>N</td>
<td>N₂</td>
<td>4</td>
<td>Gas, cal</td>
<td>Minkoff et al. (1959)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2</td>
<td>Gas, cal</td>
<td>Broida and Lutes (1956)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.03</td>
<td>γ, ESR</td>
<td>Wall et al. (1959a)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt;0.03</td>
<td>Gas, cal</td>
<td>Fontana (1958)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.001-0.04</td>
<td>Gas, MS</td>
<td>Fontana c</td>
</tr>
<tr>
<td>OH (?</td>
<td>HCOOH</td>
<td>0.2</td>
<td>γ, ESR</td>
<td>Matheson and Smaller (1955)</td>
</tr>
<tr>
<td>CH₃</td>
<td>CH₄</td>
<td>0.14</td>
<td>γ, ESR</td>
<td>Wall et al. (1959a)</td>
</tr>
<tr>
<td>H</td>
<td>CH₄</td>
<td>0.1</td>
<td>γ, ESR</td>
<td>Wall et al. (1959a)</td>
</tr>
<tr>
<td>N</td>
<td>NH₃</td>
<td>0.1</td>
<td>Gas, ESR</td>
<td>Cole and Harding (1958)</td>
</tr>
<tr>
<td>H</td>
<td>HClO₄—H₂O</td>
<td>0.1</td>
<td>γ, ESR</td>
<td>Livingston et al. (1955)</td>
</tr>
<tr>
<td>H</td>
<td>H₂O</td>
<td>0.01</td>
<td>γ, ESR</td>
<td>Matheson and Smaller (1955)</td>
</tr>
<tr>
<td>H, NH₃(?)</td>
<td>NH₃</td>
<td>0.01</td>
<td>γ, ESR</td>
<td>Matheson and Smaller (1955)</td>
</tr>
<tr>
<td>ROH</td>
<td>Alcohols</td>
<td>~0.01</td>
<td>UV, ESR</td>
<td>D. Ingramc</td>
</tr>
<tr>
<td>H</td>
<td>H₂</td>
<td>0.0006</td>
<td>γ, ESR</td>
<td>Wall et al. (1959a)</td>
</tr>
</tbody>
</table>

* Abbreviations: gas = rapid condensation of gaseous radicals; γ = gamma ray in situ production; UV = photolytic in situ production; IR = infrared analysis; cal = calorimetry; MS = magnetic susceptibility.

b Private communication.


* Difficult to distinguish energy release by small concentrations of very energetic species vs. low energy re-arrangements of host.

Transmission Spectrum of Li/nH$_2$, d $\approx$ 10 $\mu m$

--- difference + 1.0

--- pure nH$_2$

----- Li/nH$_2$

Optical Scattering in Solid Hydrogen

Crystal Growing and Quality (p. 81)
"There is a considerable art to growing hydrogen crystals of high quality. Good crystals are always grown slowly from the melt; a rapid freeze from the gas produces snow."

Crystallite Light Scattering (p. 83)
"The reason that a good hydrogen crystal is so hard to see is its low refractive index...an estimated 1.16!
Yet a 1 mm-thick layer of hydrogen crystallites can be a completely opaque brown-black."

ortho- and para-hydrogen

Rotational levels of free hydrogen molecule

\[ \begin{align*}
\text{Para H}_2 & \quad I = 0 \\
\text{Ortho H}_2 & \quad I = 1
\end{align*} \]

\[ \begin{align*}
\text{Y}_00 & \quad 0 \\
509.9 \text{ K} & \quad 844.7 \text{ K}
\end{align*} \]

[\text{I.F. Silvera, Rev. Mod. Phys. 52, 393 (1980)}]
Rapid Vapor Deposition of Gram-Scale Optically Transparent pH$_2$ Solids (c1997)

Electronic Spectroscopy of B/pH₂ (d≈2 mm)

Solid pH$_2$ Thickness from IR Spectra

Absorption Intensity vs. Thickness

new values:

\[ \int A_{Q+S} d\tilde{\nu} / d_{\text{total}} = 82 \pm 2 \text{ cm}^{-2} \]

\[ \int A_{S+S} d\tilde{\nu} / d_{\text{total}} = 6.3 \pm 0.3 \text{ cm}^{-2} \]

\[ \tilde{\alpha}_{Q+S} = 4.84(\pm 0.13) \times 10^{-14} \text{ cm}^3/\text{s} \]
\[ \tilde{\alpha}_{S+S} = 0.35(\pm 0.02) \times 10^{-14} \text{ cm}^3/\text{s} \]

literature (c1960):

\[ \tilde{\alpha}_{Q+S} = 4.5(\pm ?) \times 10^{-14} \text{ cm}^3/\text{s} \]

Constant pH$_2$ Deposition Efficiency

slope through origin
= 63.9 mmol/mm
High Flux HEDM Sources

* Purchased commercial Al evaporator; PBN crucible holds \( \approx 10 \text{ g Al} \) in horizontal orientation.

* \( T_{\text{max}} = 1200^\circ \text{C} \Rightarrow P_{\text{vap}(\text{Al})} \approx 8 \times 10^{-3} \text{ torr} \Rightarrow \Phi_{\text{Al}} \approx 10^{18} \text{ #/cm}^2\text{-s} \)

* Figure 1-3: Schematic of the EPI SUMO\textsuperscript{TM} Effusion Cell.
60 ppm Al/pH$_2$ UV Absorption (d=0.14 mm)
Al-induced IR Absorption Spectrum

Analysis in collaboration with Prof. R.J. Hinde, U. Tennessee (Knoxville).
Correlation Between UV & IR Absorptions

fitted slope = $1.96 \times 10^{-4}$
avg. ratio = $1.92 (0.21) \times 10^{-4}$

integral [IR] (cm$^{-1}$)

integral [UV] (nm)
Constant Al Atom Deposition Efficiency

![Graph showing the relationship between Al vapor pressure multiplied by deposition time (Torr-s) and integrated infrared absorption (cm⁻¹). The graph displays a linear trend with data points indicating an increase in absorption with increasing vapor pressure multiplied by deposition time.]
UV Spectrum of Recombined Al/pH₂
Recombination/reaction in Al/pH$_2$
Summary of Al/pH$_2$ Deposition Results

- catastrophic recombination observed at
  $\dot{R} \sim 200$ nm/s
  $\Phi_{H_2} \sim 50$ mmol/hr
1000 ppm Al/Ar

* Evaporate Al from 1 mm dia. Ta filaments

![Graph showing D2 and W lamp emissions]

Al atoms in solid Ar

\[
N_i = \frac{2.303 \ m_e \ c^2}{\pi \ e^2} \ \int A_{10} \ d\lambda \ \int f_{ik} \ d
\]

\[
\int A_{10} d\lambda = 5.4 \ \text{nm}
\]

\[
d = 4 \ \mu\text{m}
\]

\[
N_{Al} = 2.8 \times 10^{19} \ \#/\text{cm}^3
\]

\[
C_{Al} = 0.1 \%
\]

\[
\Delta t = 13 \ \text{min}
\]

\[
\Phi_{Al} = 1.5 \times 10^{13} \ \#/\text{cm}^2\cdot\text{s}
\]

@ \text{R} = 5 \ \text{cm}
Al/pH$_2$ Summary

* Demonstrated trapping of $\approx 0.1$ % Al atoms in thin Ar solids using home-made Al atom source.

* Demonstrated Al-induced IR absorption by pH$_2$ molecules as a diagnostic of Al atom concentrations in high column density samples.

* Attempts (four to date) to exceed 0.02 % Al atom concentrations in thick pH$_2$ solids failed, resulting in catastrophic recombination (and reaction?) of the Al atoms.

* Interpretation: thick vapor deposited pH$_2$ solids impede dissipation of heat released upon atomic recombination, causing a recombination cascade. Attempt depositions of thin ($\sim 10$ $\mu$m), high Al atom concentration Al/pH$_2$ samples (worked for Ar matrices).
Is Catastrophic Recombination Ubiquitous to Rapid Vapor Deposited pH$_2$ Solids?

\[ \frac{1}{k_{\text{recomb}}} = \frac{1}{k_{\text{intrin}}} + \frac{1}{k_{\text{diff}}} \]

* $k_{\text{intrin}}$ depends on M-M interaction potential, increases with increasing well depth and range

* \(\Rightarrow\) try Mg atoms as “HEDM” dopant
  Mg-Mg and Mg-Mg$_n$ “van der Waals” interactions

M-M Diatomic Ground State Potentials

*****INCOMPLETE SLIDE*****

* Will make PLOT comparing Al-Al and Mg-Mg ground state potentials, available from open literature.

* if not too cluttered, include Li-Li, B-B potentials, too.

* shallower wells and especially weaker long-range interactions mean reduced intrinsic recombination rates, according to G. Voth.
Annealing of 10 ppm Mg/pH$_2$ (d=0.07 mm)
As-Deposited 35 ppm Mg/pH₂ (d=0.02 mm)
Contractor Support of In-House Effort

* Assignment of Al/pH$_2$ UV absorptions.
  can change calculated Al atom concentrations by factor of 2!

* Modeling of Al atom induced IR absorptions

* Modeling of Mg recombination in solid pH$_2$ (?)

* Open Discussion:
  coordination of efforts
  other suggestions?
Recommendations for Future Experiments

* In-House:
  Complete Al/pH₂ and Mg/pH₂ experiments
  Compare Al vs. Mg to test effects of $k_{\text{intrin}}$
  Vary pH₂ deposition rate/sample thickness, and compare with
    Ne and Ar hosts to test $k_{\text{diff}}$
  Evaluate feasibility of rapid vapor deposition method
  Thermal B atom source SBIR project underway (B. Larson)

* AFOSR Contractors:
  Cluster Pickup and Deposition
  Deposition Directly onto lHe II (ala Gordon)
  In-Situ Photolysis of HEDM Precursors (Apkarian, Stwalley)
  Open Discussion: other suggestions?
Future Direction: Cluster Deposition (?)

Toward the Production of Measurable Quantities of Highly Doped Solid Hydrogen

High Energy Density Matter Contractors Conference
June 4-7, 1995

Berton Callicott, Kenneth C Janda, V. A. Apkarian, R. B. Gerber
Zhiming Li, P. Taborek and J. Rutledge
Advanced Cryogenic Materials Group
University of California
Irvine, California

The goal of this effort is to produce measurable quantities of highly doped (5-10%) solid hydrogen. The desired dopant atoms are C, B, O, and N. Our approach to this material is via the cluster deposition technique, as illustrated in Figure 1. First, a beam of large He clusters (between $10^4$ and $10^5$ He atoms per cluster) is created following the methods of Toennies$^1$ and Scoles.$^2$ Next, the He clusters are passed through a scattering chamber that contains hydrogen molecules and, in the process, “pick-up” between 12 and 20 hydrogen molecules. During the pick up process, sufficient He atoms evaporate for the cluster to maintain a temperature of about 1 K, and the hydrogen is expected to make a small micro-crystal within the He cluster. Next, the He cluster picks up the desired dopant atom. Again, He atoms evaporate to cool the cluster back to 1 K.

* Most excess heat is dissipated before the clusters are deposited.
* Chance to beat the “statistical limit” of stored atom concentration.
* Either higher fluxes or UHV deposition environment required.
Future Direction: Deposition onto lHe II (?)

Based on E.B. Gordon’s work

“Big-Flush” (c1995)

CESE discharge of N₂/He

Optical emission was only diagnostic (N/D₂ samples didn’t glow!)

Need alternative (species specific) experimental diagnostics: ESR, NMR, FIR absorption… (?)
Future Direction: In-Situ Photolysis (?)

* V.A. Apkarian, et al. experiments (c1994):

\[ \text{O}_2/D_2 + h\nu \rightarrow \text{O}/D_2 + ? \]

(5% O/H\(_2\) \(\Rightarrow\) 25s (6%) I\(_{sp}\) improvement, so Al > O > H)

UV induced desorption of H\(_2\)O inside vacuum chamber complicates monitoring Õ + H\(_2\) reactions.

* W.C. Stwalley proposal (c1992):

\[ \text{M} + h\nu \quad \rightarrow \quad \text{M}^* \]
\[ \text{M}^* + \text{H}_2 \quad \rightarrow \quad \text{MH} + \text{H} \]
\[ \text{MH} + h\nu' \quad \rightarrow \quad \text{M}^* + \text{H} (\text{cold}) \]
\[ \text{M}^* \quad \rightarrow \quad \text{M} + h\nu'' \]
\[ \text{H}_2 + h\nu + h\nu' \quad \rightarrow \quad 2\text{H} + h\nu'' \quad \text{(net reaction)} \]
Experimental Admonitions

* Must work with hydrogen! Some efforts on model systems are fine, but results may not generalize cleanly to hydrogen.

* Must focus on production and quantitative measurement of $\sim 1\%$ concentrations of energetic species in solid hydrogen. Species specific diagnostics are preferred.

* Worry about scaling up later, must demonstrate progress towards larger concentrations to maintain viability of Cryosolid Propellants Task.