**REPORT DOCUMENTATION PAGE**

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<th>3. DATES COVERED (From - To)</th>
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| b. ABSTRACT                                            |
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| c. THIS PAGE                                           |
| Unclassified                                           |
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| 17. LIMITATION OF ABSTRACT                             |
| A                                                      |

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Standard Form 298 (Rev. 9-98) 
Prepared by ANSI Std. 239.18
MEMORANDUM FOR PRS (Contractor/In-House Publication)

FROM: PROI (TI) (STINFO) 23 June 1999

M.E. Fajardo and S. Tam, "Rapid Vapor Deposition on Millimeters Thick Optically Transparent Parahydrogen Matrices"

Gordon Research Conference (International) (Statement A)
Rapid Vapor Deposition of Millimeters Thick Optically Transparent Parahydrogen Matrices

Mario E. Fajardo and Simon Tam
US Air Force Research Laboratory, Propulsion Directorate (AFRL/PRSP Bldg. 8451, Edwards AFB, CA 93524-7680) mario_fajardo@ple.af.mil

High Energy Density Matter (HEDM) Cryosolid Propellants
UV/Vis Spectroscopy of Li & B Atoms in Solid Hydrogen
Rapid Vapor Deposition of Thick Parahydrogen (pH$_2$) Matrices
IR/Raman Spectroscopic Characterization of Pure pH$_2$ Solids
Dopant-induced IR Activity in pH$_2$ Solids (the “solvent” speaks)
High Resolution IR Spectroscopy in Vapor Deposited pH$_2$ Solids

Summary and Future Directions

DISTRIBUTION STATEMENT A
Approved for Public Release
Distribution Unlimited
HEDM Cryosolid Propellants Payoffs

Increased Specific Impulse

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

LOX/LH\(_2\) : \( I_{sp} = 390\) s
5\% B/sH\(_2\) + LOX : \( I_{sp} = 500\) s (+30\%)*

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

Greater Propellant Density

liquid H\(_2\) @ 20 K : \( \rho = 0.070\) g/cm\(^3\)

solid H\(_2\) @ 2 K : \( \rho = 0.087\) g/cm\(^3\) (+25\%)
50/50 liquid He/solid H\(_2\) : \( \rho = 0.105\) g/cm\(^3\) (+50\%)
HEDM dopant recombination/reaction

* ideally:

\[ X + p\text{H}_2 \xrightarrow{T=2K} X/p\text{H}_2 \]

isolated atoms

* in practice:

\[ X + X + M \rightarrow X_2 + M \rightarrow X_n \]

recombination

\[ X + H_2 + M \rightarrow HX + H + M \rightarrow H_nX + M \]

reaction

\[ X_n + H_2 + M \rightarrow HX_n + H + M \rightarrow H_mX_n + M \]

both
Scientific/Technological Motivations

<table>
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<tr>
<th>Issue</th>
<th>Scientific Motivation</th>
<th>Tech. Application</th>
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<tr>
<td>Chemical stability of M/pH₂ samples</td>
<td>Chemical reactivity @ low T (1-10 K)</td>
<td>Identify candidate M’s</td>
</tr>
<tr>
<td></td>
<td>← existence of small reaction barriers in M + H₂ reaction</td>
<td></td>
</tr>
<tr>
<td></td>
<td>← matrix host effects</td>
<td></td>
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<tr>
<td>Microscopic model of sample deposition process</td>
<td>Molecular dynamics of “simple” condensed phase systems (models for more complicated chemistry)</td>
<td>Maximize [M]</td>
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<tr>
<td>Simulation of M/RGS and M/pH₂ spectroscopy</td>
<td>Spectroscopy in condensed phases</td>
<td>Measure [M] and determine fuel ρ</td>
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<tr>
<td></td>
<td>← spectrum ↔ structure/fluctuations</td>
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<tr>
<td>Diffusion/recombination of M’s</td>
<td>Diffusion in “classical” and “quantum” solids</td>
<td>Determine thermal stability of M/H₂ fuel</td>
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<tr>
<td>Maximum attainable [M]</td>
<td>Limits of chemical energy storage</td>
<td>fuel performance</td>
</tr>
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</table>
Experimental Diagram (c. 1993)

LAMP

source

mono

Cryo

HeNe

Laser Ablation
Li/H$_2$ \( T=3K \)

B/H2 raw data (c1993)

\[ \approx 5\% \text{ absorption } \lambda \approx 10\mu \]

\[ T \approx 2K \]
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\,\mu\text{m}-thick layer of hydrogen crystallites can be a completely opaque brown-black."

P.C. Souers,

*Hydrogen Properties for Fusion Energy*

Deposition Cartoon

gas phase — accretion layer — solid hydrogen
Ortho and Para Hydrogen

Rotational levels of free Hydrogen molecule

\[ J \quad (2J+1) \]

Para \( H_2 \)  
I = 0  
509.9 K

Ortho \( H_2 \)  
I = 1  
170.5 K

\[ Y_{00} \]

I.F. Silvera,  
Rev. Mod. Phys. 52, 393 (1980).
Experimental Diagram (c1997)

UV Transmission of 1-mm Thick B/pH$_2$ Sample
B/pH$_2$ LIF

$\lambda_{exc} = 207, 210, 217, \text{and } 220 \text{ nm}$
B/pH₂ LIF Cartoon

potential energy

blue-shifted absorption

un-shifted emission

B₂s²3s(^2S)

B₂s²2p(^2P°)

configurational coordinate
IR Absorption of 6 mm Thick Parahydrogen Solid

$T = 2 \text{ K.}$

Non-observation of the $Q_1(0)$ transition ($4153 \text{ cm}^{-1}$) demonstrates the absence of $\text{oH}_2$ impurities, and that the microscopic structure is not amorphous or porous.

Observation of $S_1(0)$ transition demonstrates the absence of inversion symmetry for some $\text{H}_2$ molecular environments.

[J. van Kranendonk and H.P. Gush, Phys. Lett. 1, 22 (1962)]
Raman Spectra of 4.5 and 6 mm Thick Parahydrogen Solids

Mixed hcp/fcc as-deposited structure, anneals to hcp; compare with:


(d) sample in (c) warmed to 4.5 K.
(c) 4.5 mm sample as deposited at 3.3 K (Φ = 290 mmol/hr).

(b) sample in (a) warmed to 4.5 K.
(a) 6 mm sample as deposited at 3.1 K (Φ = 200 mmol/hr).

(Thanks, Ingrid!)
charged dopant
induced H₂ absorptions

absorbance (arb.)

wavenumber (cm⁻¹)

2% O/H₂

Mg/H₂

Al/H₂

Sc/H₂

p-H₂
High Resolution IR Spectroscopy in Solid pH$_2$

T. Momose, K.E. Kerr, D.P. Weliky, C.M. Gabryls, R.M. Dickson and T. Oka,

FIG. 1. Apparatus for the simultaneous spectroscopy of the infrared and Raman transitions. The nonlinearity of LiNbO$_3$ is used for the former and that of solid H$_2$ is used for the latter. D.M., dichroic mirror; S. A., spectrum analyzer; P. B., polarizer beamsplitter.
$v_4 \text{CH}_4/p\text{H}_2$ absorptions

\begin{align*}
\text{as-dep} \\
T=2.4K
\end{align*}

\begin{align*}
\log_{10}(l/l) \\
2.4K
\end{align*}

\begin{align*}
\text{log}_{10}(l/l) \\
3.6K
\end{align*}

\begin{align*}
\text{log}_{10}(l/l) \\
4.8K
\end{align*}

\begin{align*}
\text{log}_{10}(l/l) \\
2.4K
\end{align*}

wavenumber (cm$^{-1}$)
$v_4$ CH$_4$/pH$_2$ Absorptions

![Graphs showing absorption spectra at different transition levels: P(1), Q(1), R(0), R(1) at various wavelengths.](image)
CH$_4$/pH$_2$ Energy Levels

88 PPM HCl/pH₂  d≈3mm

st27061.11 annealed  T=2.4K
st27061.7  as deposited T=2.4K
resolution = 0.0075 cm⁻¹
irreversible T dependences

88 PPM HCl/pH₂ d=3mm
st27061.7 as deposited T=2.4K
st27061.11 annealed T=2.4K
reversible T dependences

st27103.13 evaporating $T \approx 10\,\text{K}$
st27103.4 annealing $T = 4.8\,\text{K}$
st27061.11 annealed $T = 2.4\,\text{K}$

94 PPM H$_{37}$Cl
gas phase HCl and (HCl)_2 transitions
(HCl)$_2$ $\nu_2^+$ region

st27061.11 annealed  T=2.4K  88 PPM HCl
st27097.6  annealed  T=2.4K  33 PPM $^{37}$Cl
st27073.17  annealed  T=2.4K  30 PPM $^{35}$Cl
$v_0$, $v_1$, $v_2$ gas phase energy levels
for (H$^{35}\text{Cl})_2$, H$^{35}$ClH$^{37}$Cl, and (H$^{37}\text{Cl})_2$
123 PPM HF/pH$_2$  d$\approx$3mm

st27115.15  annealed  T=2.4K
st27115.13  annealing  T=4.8K
st271215.9  as deposited T=2.4K  resolution = 0.005 cm$^{-1}$
260 PPM HBr/pH₂  d≈3mm

st27145.9  annealed  T=2.4K
st27145.7  annealing  T=4.8K
st27145.5  as deposited T=2.4K  resolution = 0.005 cm⁻¹
(HBr)$_2$/pH$_2$

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<th>Sample</th>
<th>Condition</th>
<th>Temperature (K)</th>
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<td>T=2.4K</td>
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<tr>
<td>st27140.7</td>
<td>annealing</td>
<td>T=4.8K</td>
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<tr>
<td>st27140.5</td>
<td>as deposited</td>
<td>T=2.4K</td>
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80 PPM HBr/pH$_2$ d≈3mm

resolution = 0.005 cm$^{-1}$
HCl-(HF, HCl, HBr)/pH$_2$

- st27145.9  annealed  T=2.4K
- st27145.7  annealing  T=4.8K
- st27145.5  as deposited  T=2.4K

260 PPM HBr/pH$_2$  d=3mm  resolution = 0.005 cm$^{-1}$
1 PPM CO$_2$/pH$_2$, d≈3mm

- st27025.11, annealed, T=2.4K
- st27025.9, annealing, T=4.8K
- st27025.7, as deposited, T=2.4K

Resolution = 0.005 cm$^{-1}$
\( \nu_3 \text{CO}_2/(\text{HCl})_n \) clusters

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<th>State</th>
<th>Temperature</th>
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<td>494 PPM HCl</td>
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<td>94 PPM H(^{37})Cl</td>
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<td>st27085.9</td>
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<td>284 PPM H(^{35})Cl</td>
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HEDM Cryosolids Accomplishments
(a list of "things that’ll never work.")

* Trapped Li, B, Na, Mg, Al atoms in solid hydrogen.

* Demonstrated production of gram-scale transparent pH$_2$ solids by rapid vapor deposition.

* Demonstrated that vapor deposited pH$_2$ solids are densest close-packed solids, NOT amorphous.

* Generalized phenomenon of dopant induced IR activity in pH$_2$ host; diagnostic for thick, concentrated samples.
Summary and Future Directions

* Demonstrated suitability of rapid vapor deposited pH$_2$ solids as hosts for high-resolution IR MIS.
  CH$_4$/pH$_2$(fcc) & CH$_4$/pH$_2$(hcp) [w/T. Momose]
  HCl monomers nearly free rotors,
  $B_{\text{HCl/pH}_2} \approx 10.4 \text{ cm}^{-1}$ (vs. 10.6 cm$^{-1}$ gas phase)
  HCl dimer does not rotate end-over-end
  (?) for H$^{35}$Cl-H$^{37}$Cl dimer, $v_2=1$ interconversion splitting $\approx 2.3 \text{ cm}^{-1}$ (vs. 3.732 cm$^{-1}$ gas phase)

* Evaluate/develop theoretical absorption models
  crystal field theory
  rotation-translation coupling (RTC) model
  spectroscopy of "pendular" states
  quantum Monte Carlo spectral simulations