

REPORT DOCUMENTATION PAGE

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MEMORANDUM FOR PRS (In-House Publication)

FROM: PROI (STINFO)

11 May 2001

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2001-115**
Mario Fajardo and Michelle DeRose, "Status of Cryosolid Propellants Task"

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

(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.

Comments: _____

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Comments: _____

APPROVED/APPROVED AS AMENDED/DISAPPROVED

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 (pH₂) Solids
- * Update on Al/pH₂ and Mg/pH₂ 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. Dagdigan @ 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/LH₂:

LOX/LH₂ $\Delta H_{sp} = 12.6 \text{ MJ/kg}$ (3.0 kcal/g)

HEDM Target: $\Delta H_{sp} > 15.0 \text{ MJ/kg}$ (3.6 kcal/g)

* Early (c1990) Revolutionary HEDM Concepts:

tetrahydrogen (H₄)

metastable triplet helium (He* and He₂*)

spin-polarized atomic hydrogen (H↑)

high-spin species (⁵CO)

dications (AB⁺⁺, ABC⁺⁺⁺)

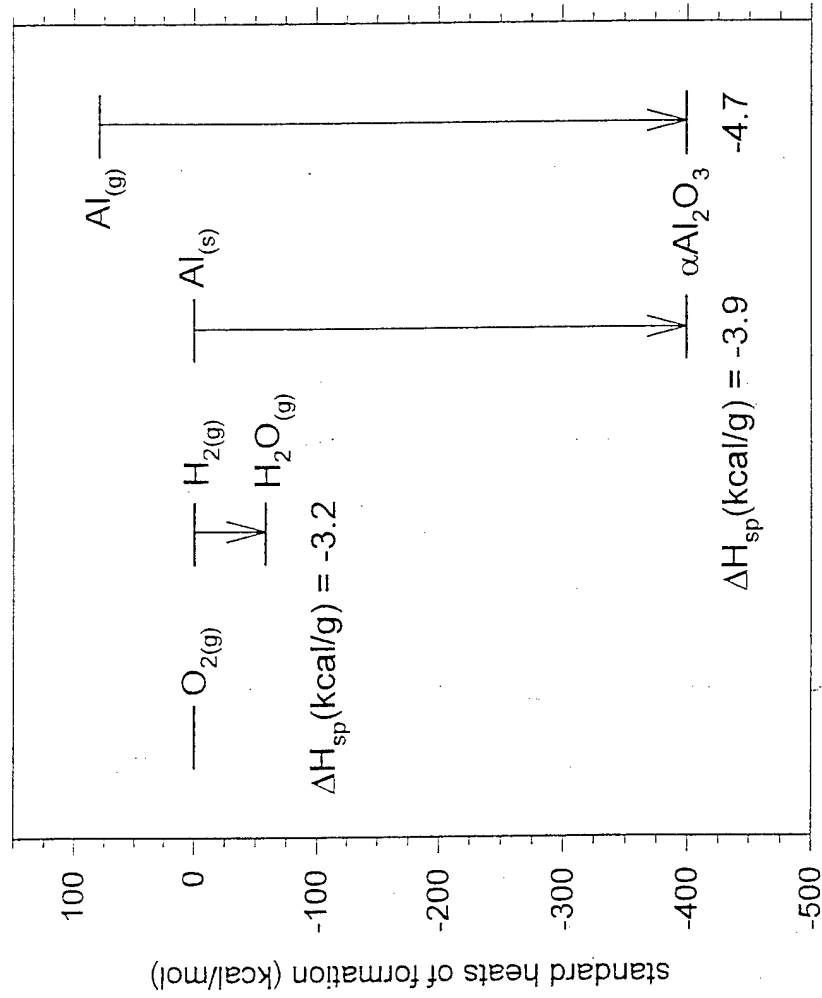
♥ “non-metallics” (e.g. O₄/H₂, N₄, N₈, N₂₀)  N₅⁺!

metallic hydrogen

♥ metal atoms and clusters in solid H₂

Cryosolid Propellants Concept

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



Cryosolid Propellants Payoffs

Increased Specific Impulse

$$I_{sp} \propto \sqrt{\Delta H_{sp}}$$

$$\text{LOX/LH}_2 : I_{sp} = 400 \text{ s}$$

$$5\% \text{ B/sH}_2 + \text{LOX} : I_{sp} = 500 \text{ s (+25%)*}$$

$$5\% \text{ Al/sH}_2 + \text{LOX} : I_{sp} = 450 \text{ s (+12%)*}$$

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

Greater Propellant Density

$$\text{liquid H}_2 @ 20 \text{ K} : \rho = 0.070 \text{ g/cm}^3$$

$$\text{solid H}_2 @ 2 \text{ K} : \rho = 0.087 \text{ g/cm}^3 (+25\%)$$

$$50/50 \text{ liquid He/solid H}_2 : \rho = 0.105 \text{ g/cm}^3 (+50\%)$$

Atom Additive Payoffs (5 % molar)

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

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

Additive	in standard state		as atoms		monoprop.	
	<u>M(5%)/LOX/H₂</u>		<u>M(5%)/LOX/H₂</u>		<u>M(5%)/H₂</u>	
none	403					
C	381 (-5%)		515 (+28%)		515 (+28%)	
B	407 (+1%)		508 (+26%)		465 (+15%)	
Be	427 (+6%)		493 (+22%)			
Si	400 (-1%)		460 (+14%)			
Al	407 (+1%)		454 (+13%)			
H	403		430 (+7%)		380 (-6%)	
Li	404		428 (+6%)			
Mg	400 (-1%)		416 (+3%)			

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 $\sim 1 \text{ cm}^3$ samples in our lab.

Example: 5% Al/pH₂, $V = 1 \text{ cm}^3$

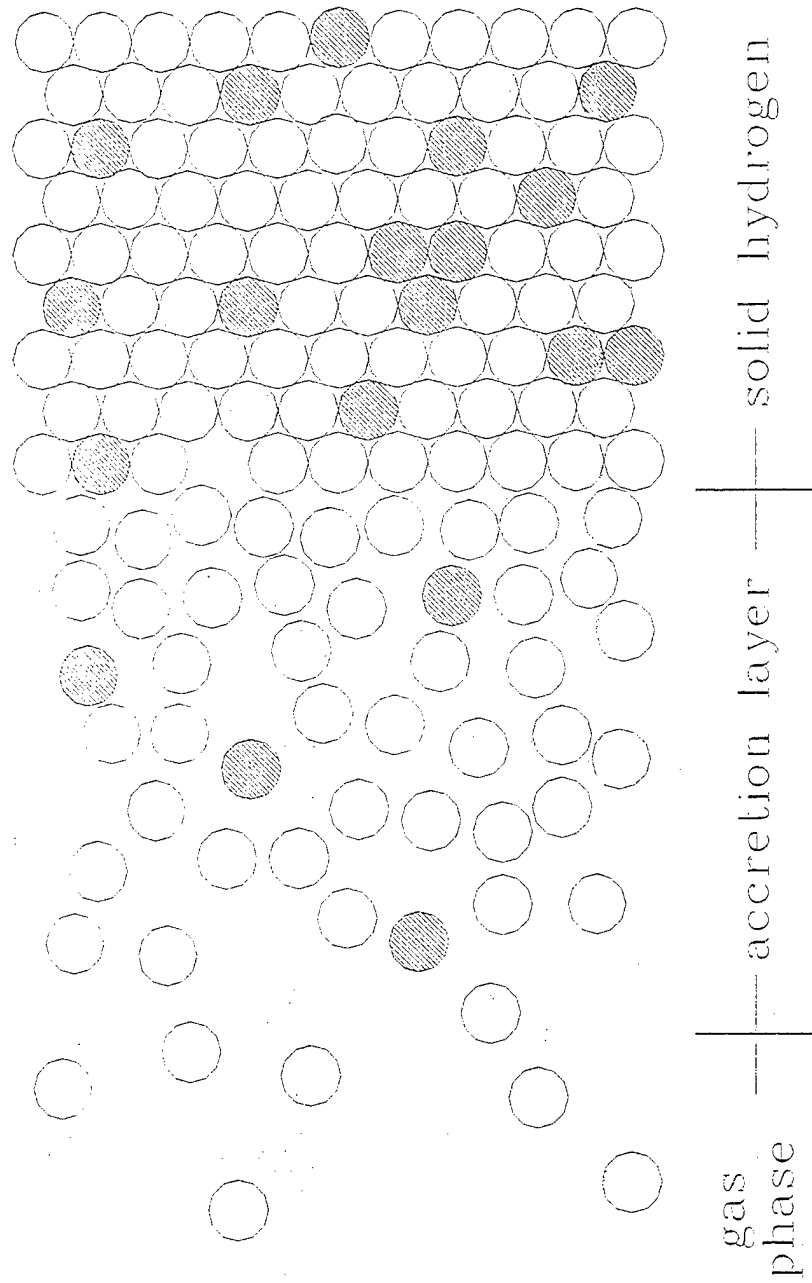
assume each Al atom replaces one H₂ molecule

$\Rightarrow 58 \text{ mg Al} / 83 \text{ mg H}_2$ (*see display item*)

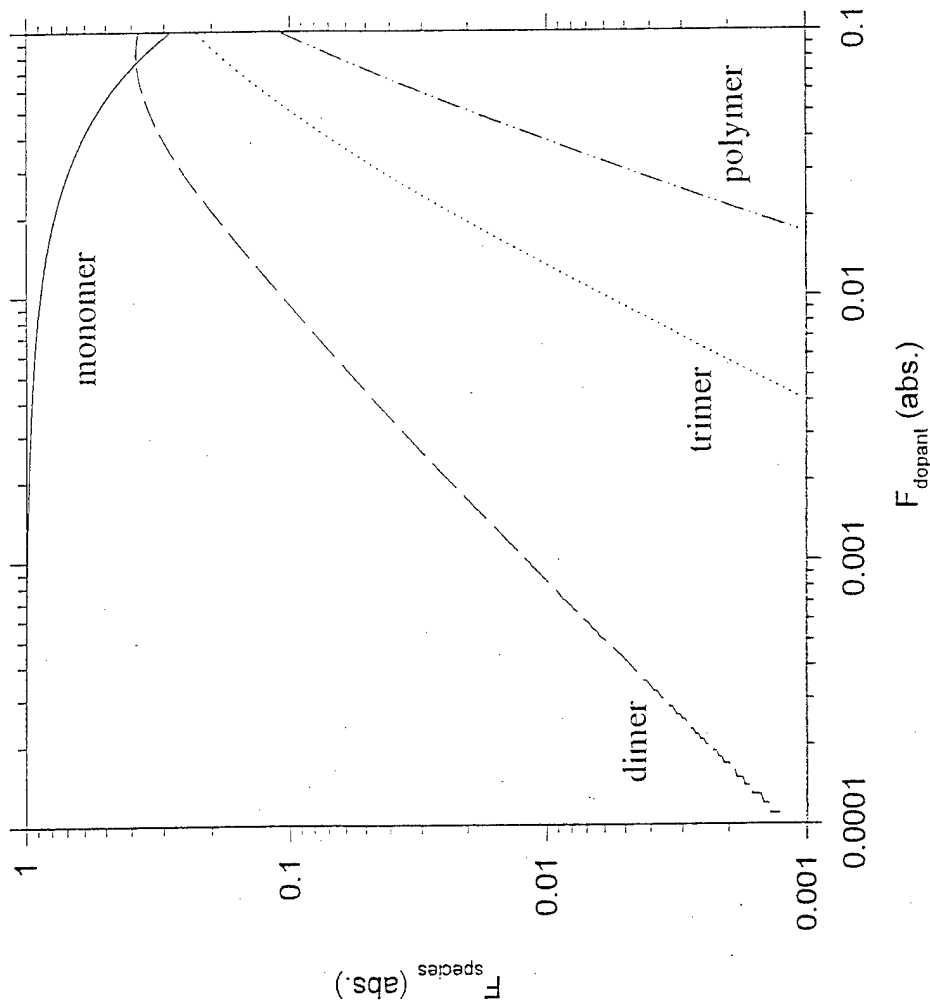
$\therefore \rho = 0.142 \text{ g/cm}^3$ (+100%)

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: $A = \sigma N d$
 $A = \text{absorbance} = -\ln(I/I_0)$
 $\sigma = \text{absorption cross-section}$
 $N = \text{species number densities}$
 $d = \text{pathlength}$
 $N d = \text{"column density"}$
- * 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

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GEORGE C. PIMENTEL

TABLE IX
CONCENTRATIONS OF FREE RADICALS REPORTED

Radical	Matrix	Mole per cent radicals	Method of production and estimate ^a	Reference
O	O ₂	4-20 <3 ~1	Gas, cal Gas, IR Gas, cal	Minkoff <i>et al.</i> (1959). Harvey and Bass (1958) Broida and Lutes (1956)
OH	C ₂ (OH) ₂	0.6	γ, ESR	R. Livingston ^b
N	N ₂	4	Gas, cal	Minkoff <i>et al.</i> (1959)
		0.2	Gas, cal	Broida and Lutes (1956)
		0.03	γ, ESR	Wall <i>et al.</i> (1959b)
		>0.03	Gas, cal	Fontana ^c (1958)
		0.01-0.04	Gas, MS	Matheson and Smaller (1955)
OH(?)	HCOOH	0.2	γ, ESR	Wall <i>et al.</i> (1959a)
CH ₃	CH ₄	0.14	γ, ESR	Wall <i>et al.</i> (1959a)
H	CH ₄	0.1	γ, ESR	Cole and Harding (1958)
N	NH ₃	0.1	Gas, ESR	Livingston <i>et al.</i> (1955)
H	HClO ₄ -H ₂ O	0.1	γ, ESR	Matheson and Smaller (1955)
H, NH ₂ (?)	H ₂ O	0.01	γ, ESR	Matheson and Smaller (1955)
ROH	NH ₃	0.01	γ, ESR	D. Ingram ^b
H	Alcohols	~0.01	UV, ESR	Wall <i>et al.</i> (1959a)
	H ₂	0.0006	γ, ESR	

^a 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.

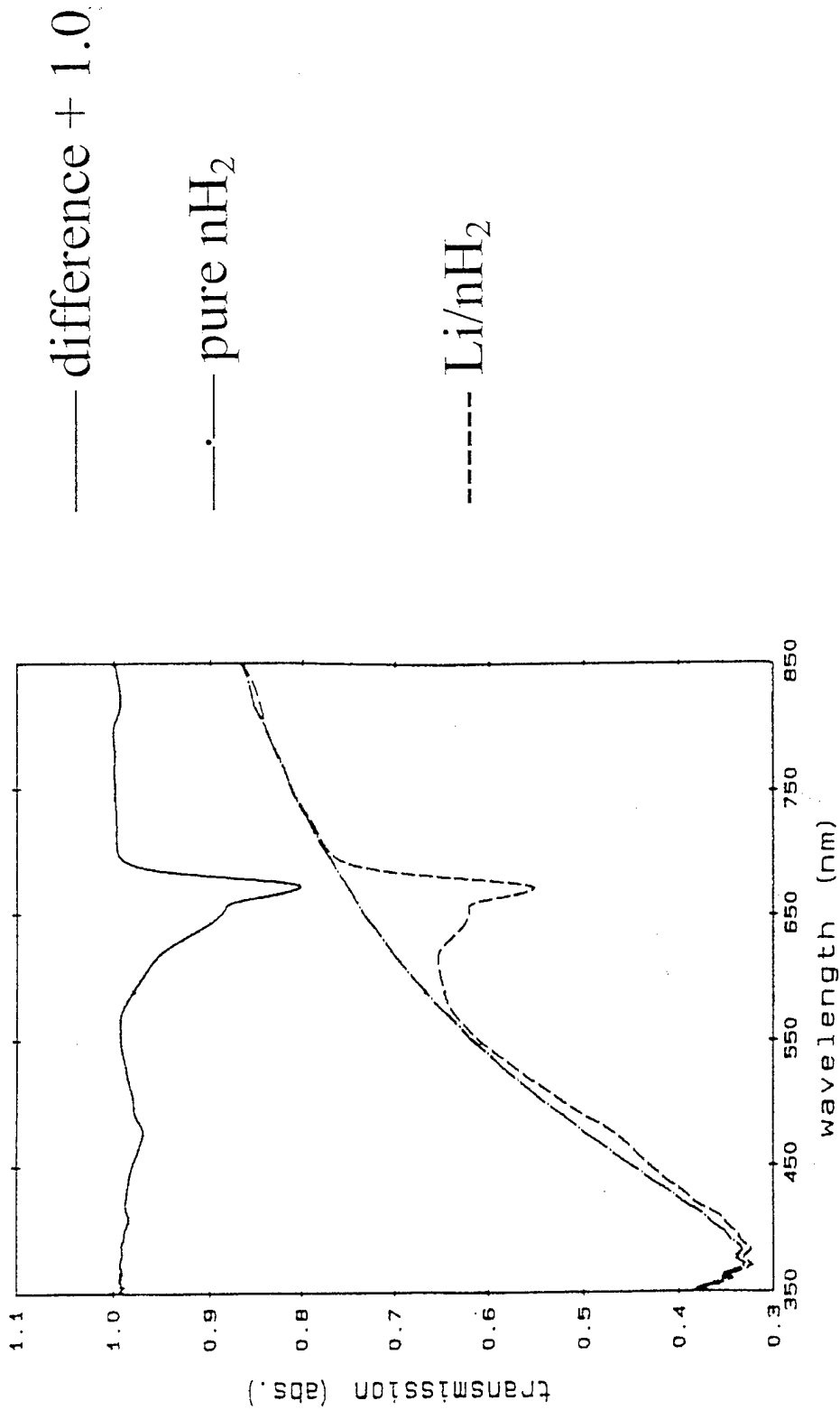
^b Private communication.

^c Fontana, B. J. (1959). *J. Chem. Phys.* **31**, 148.

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

[A.M. Bass and H.P. Broida, "Formation and Trapping of Free Radicals" (Academic, New York, 1960)]

Transmission Spectrum of Li/nH_2 , $d \approx 10 \mu$



M.E. Fajardo, J. Chem. Phys. **98**, 110 (1993).

Optical Scattering in Solid Hydrogen

Crystal Growing and Quality (p. 81)

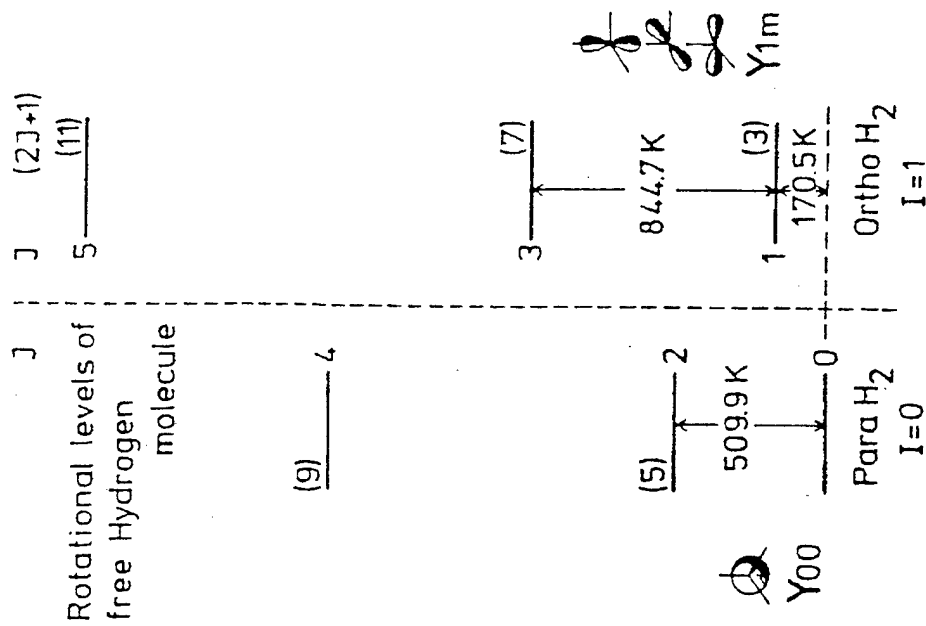
“There is a considerable art to growing hydrogen crystals of high quality. Good crystals are always grown slowly from the melt; a rapid freeze from the gas produces snow.”

Crystallite Light Scattering (p. 83)

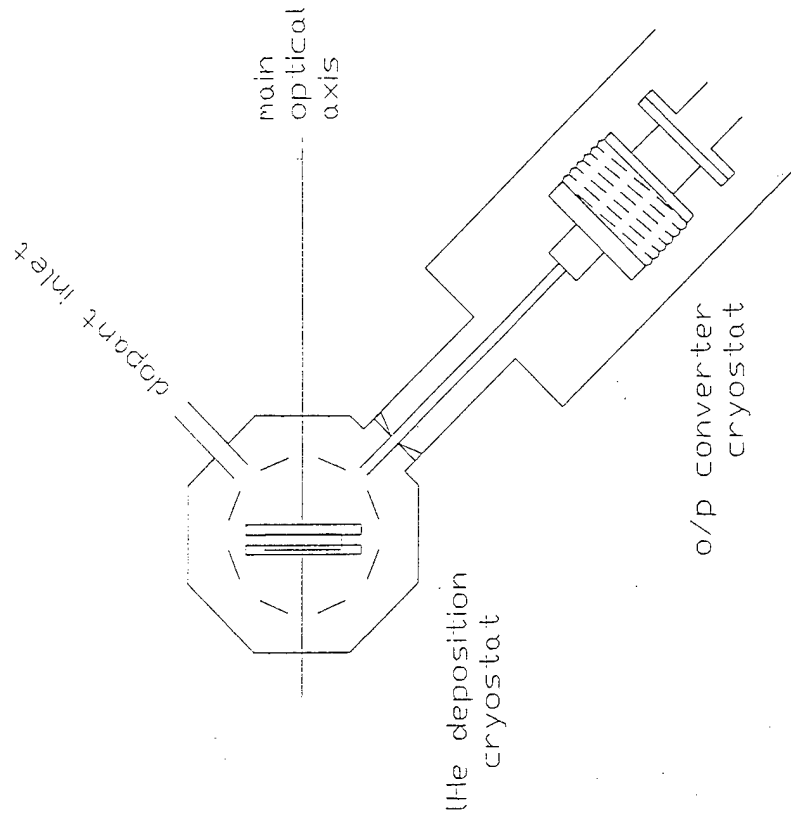
“The reason that a good hydrogen crystal is so hard to see is its low refractive index...an estimated 1.16!

Yet a 1 mm-thick layer of hydrogen crystallites can be a completely opaque brown-black.”

ortho- and para-hydrogen

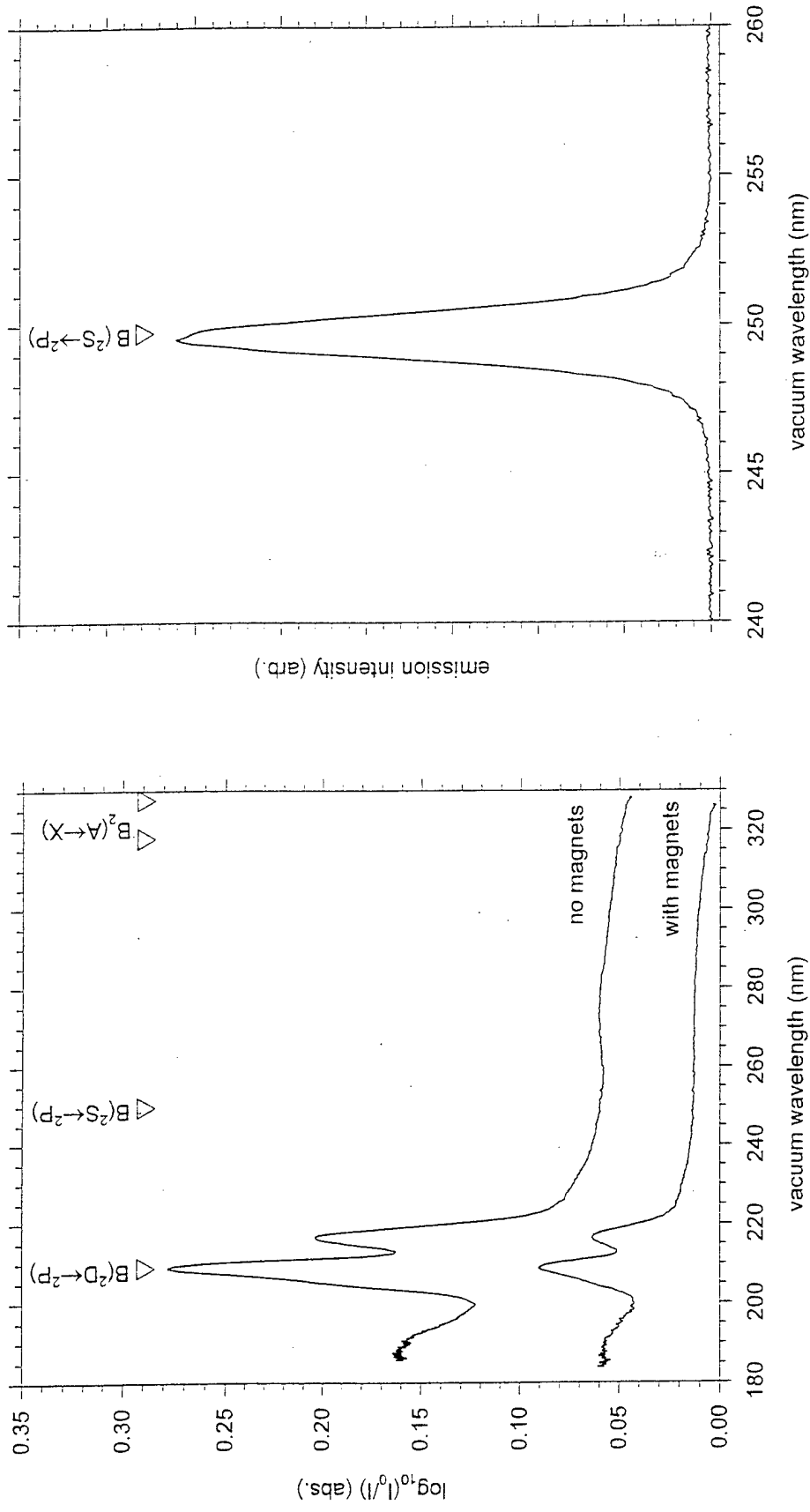


Rapid Vapor Deposition of Gram-Scale Optically Transparent pH₂ Solids (c1997)



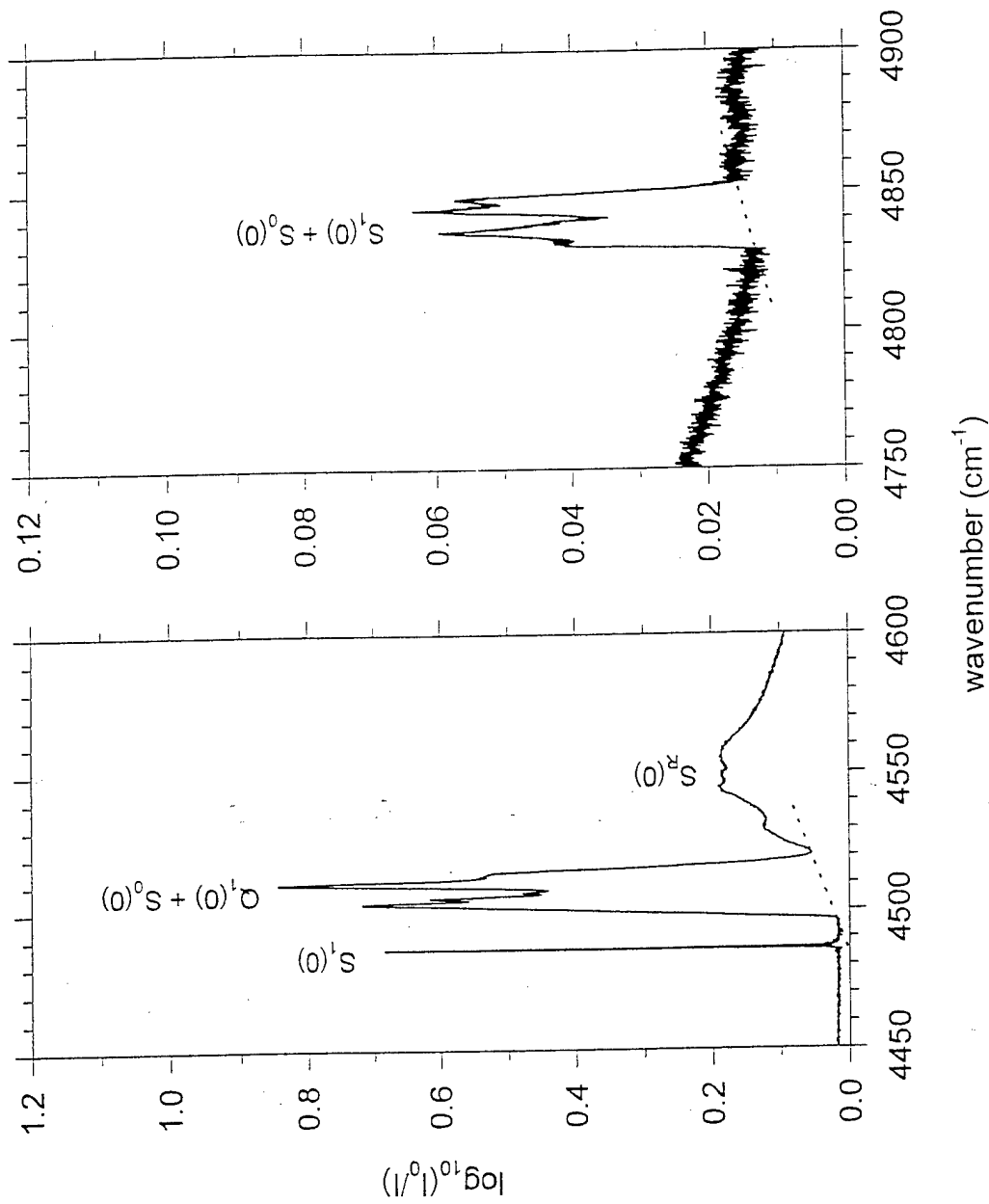
M.E. Fajardo and S. Tam, *J. Chem. Phys.* **108**, 4237 (1998).
S. Tam and M.E. Fajardo, *Rev. Sci. Instrum.* **70**, 1926 (1999).

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



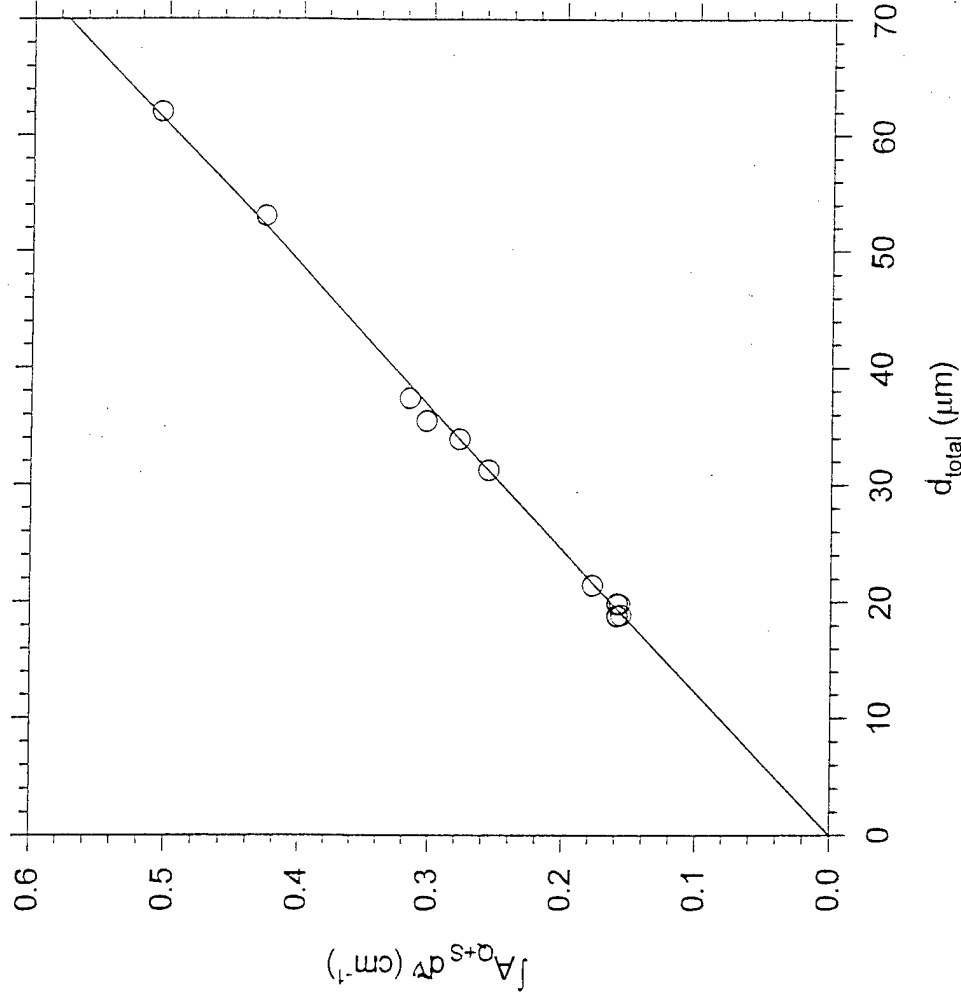
S. Tam, M. Macler, M.E. DeRose, and M.E. Fajardo, *J. Chem. Phys.* **113**, 9067 (2000).
[J.R. Krumrine, S. Jang, G.A. Voth, and M.H. Alexander, *J. Chem. Phys.* **113**, 9079 (2000)]

Solid pH₂ Thickness from IR Spectra



S. Tam and M.E. Fajardo, Rev. Sci. Instrum., submitted (2001).

Absorption Intensity vs. Thickness



new values:

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

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

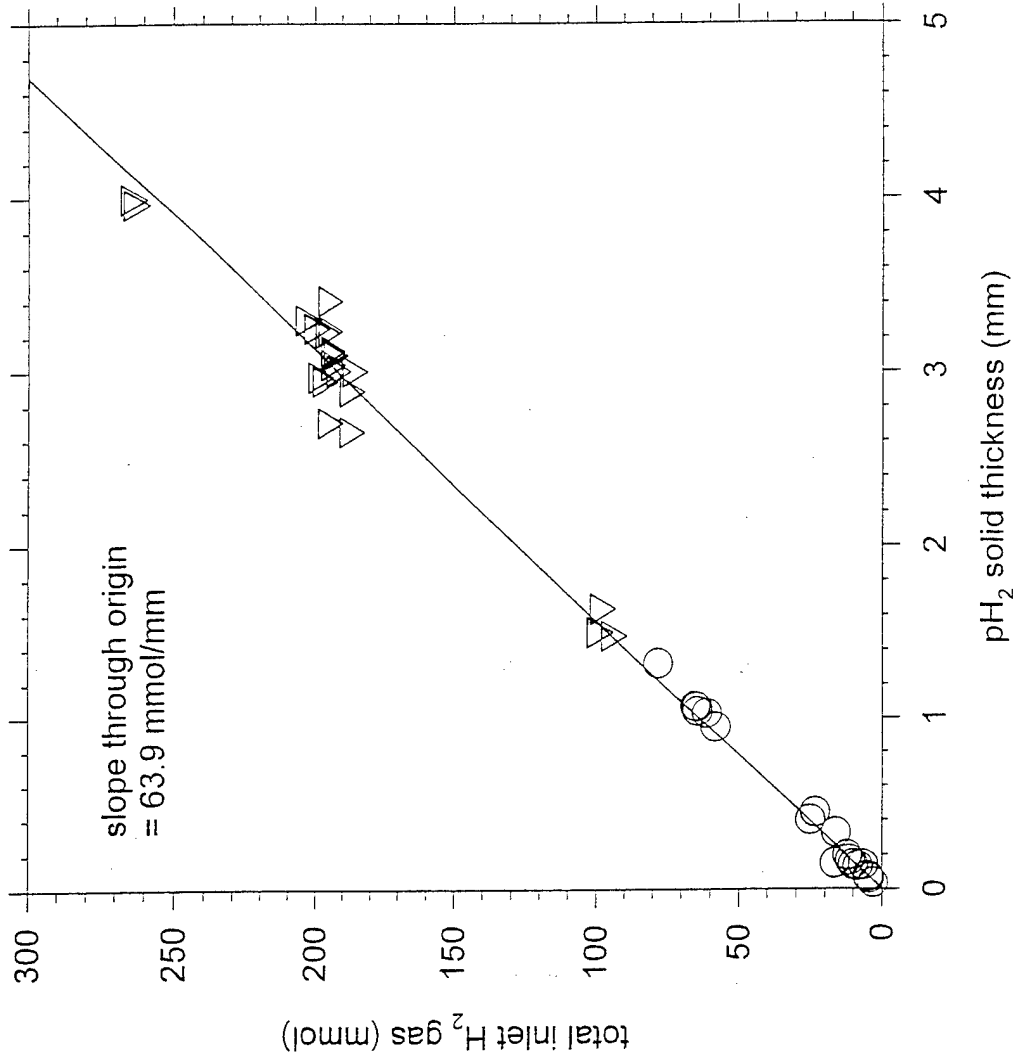
$$\tilde{\alpha}_{Q+S} = 4.84(\pm 0.13) \times 10^{-14} \text{ cm}^3/\text{s}$$

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

literature (c1960):

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

Constant pH₂ Deposition Efficiency



High Flux HEDM Sources

- * Purchased commercial Al evaporator; PBN crucible holds ≈ 10 g Al in horizontal orientation.
- * $T_{\max} = 1200$ °C $\Rightarrow P_{\text{vap}}(\text{Al}) \approx 8 \times 10^{-3}$ torr $\Rightarrow \Phi_{\text{Al}} \approx 10^{18}$ #/cm²-s

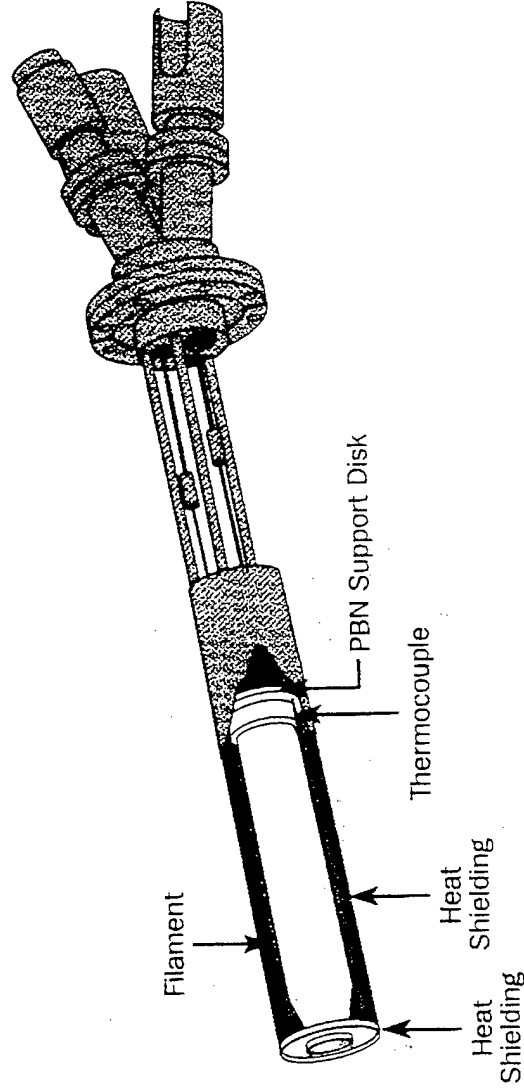
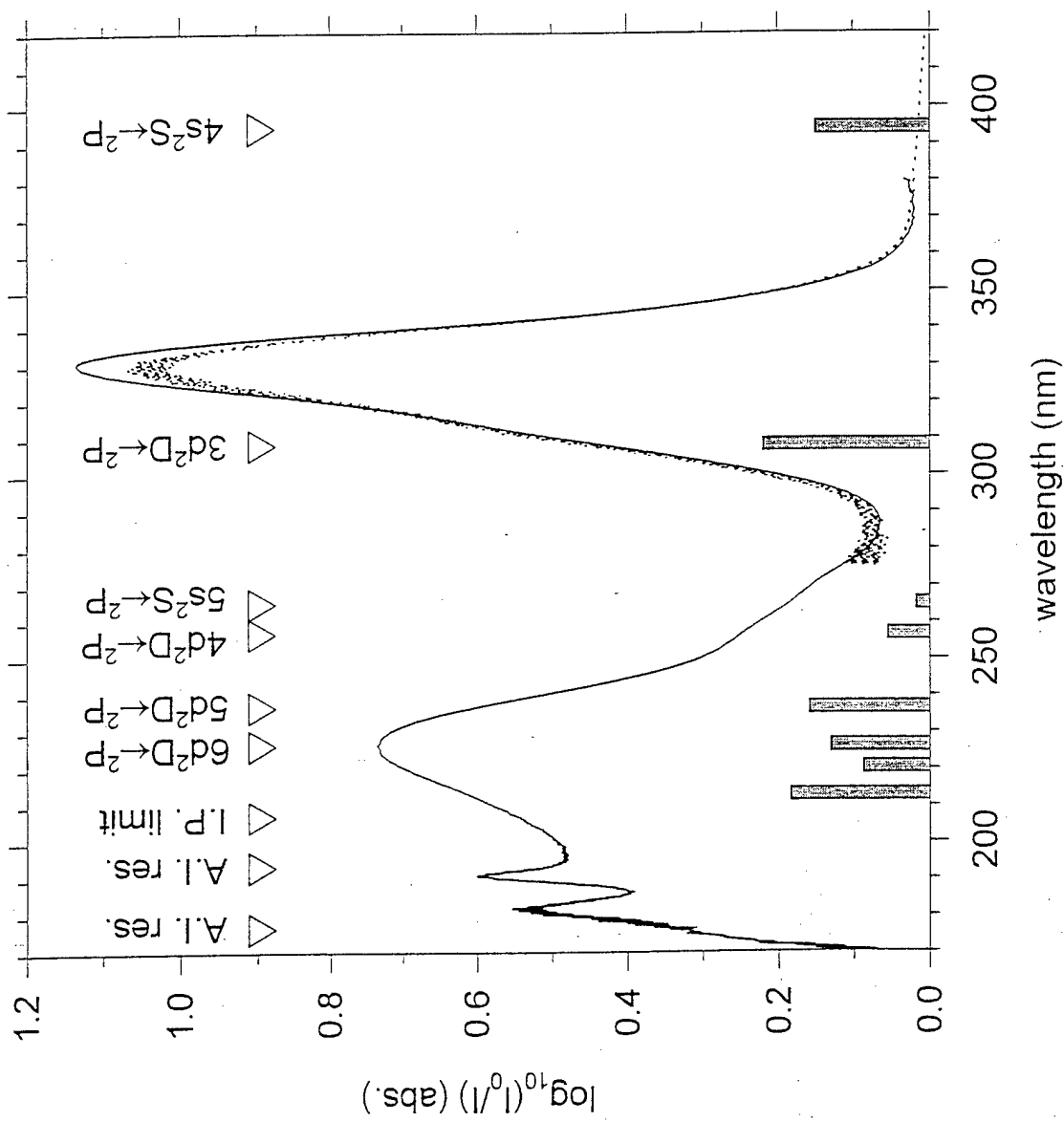
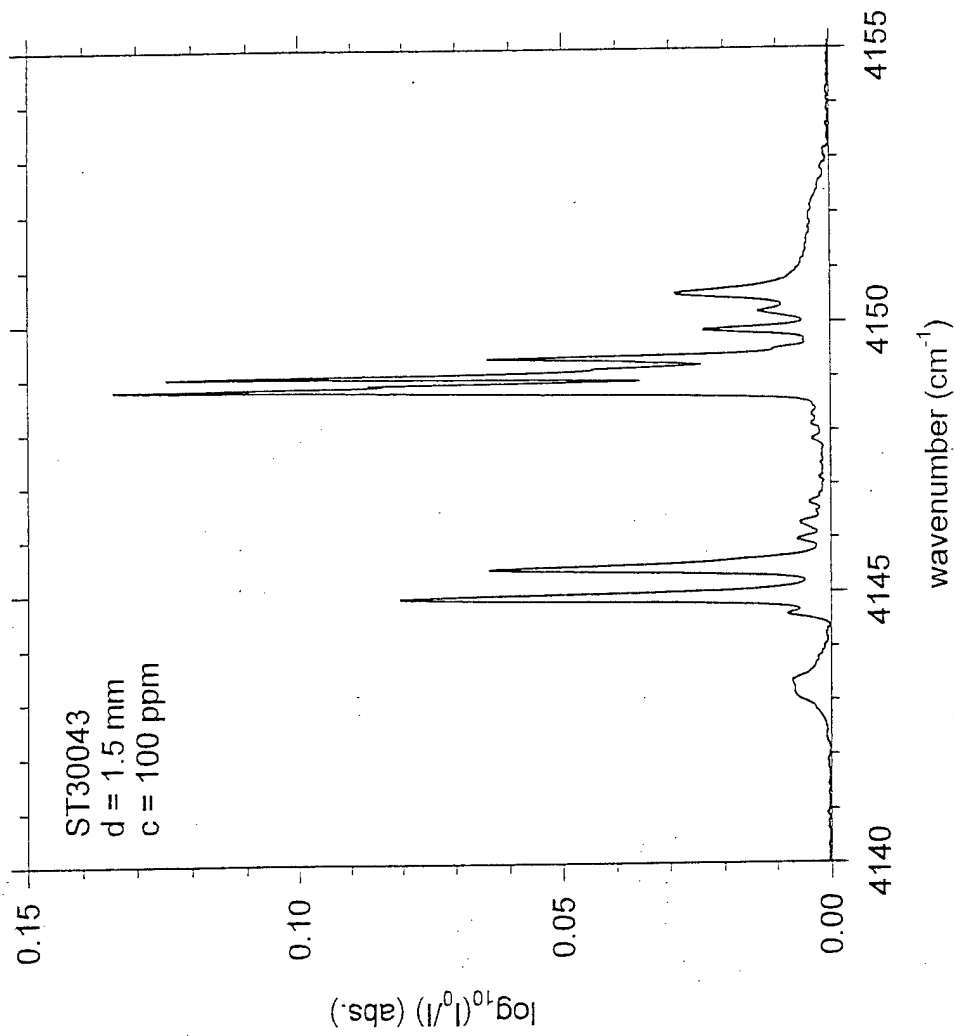


Figure 1-3: Schematic of the EPI SUMO™ Effusion Cell.

60 ppm Al/pH₂ UV Absorption (d=0.14 mm)

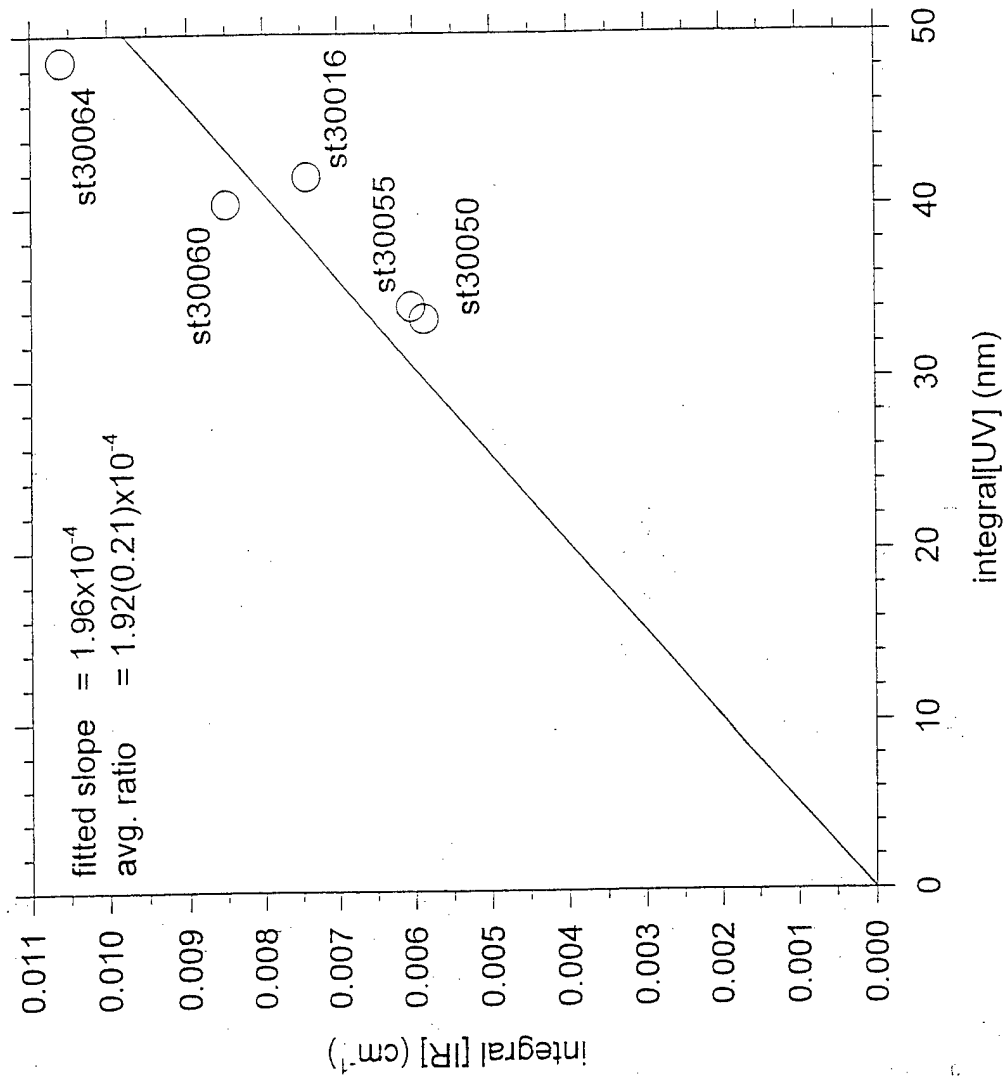


Al-induced IR Absorption Spectrum

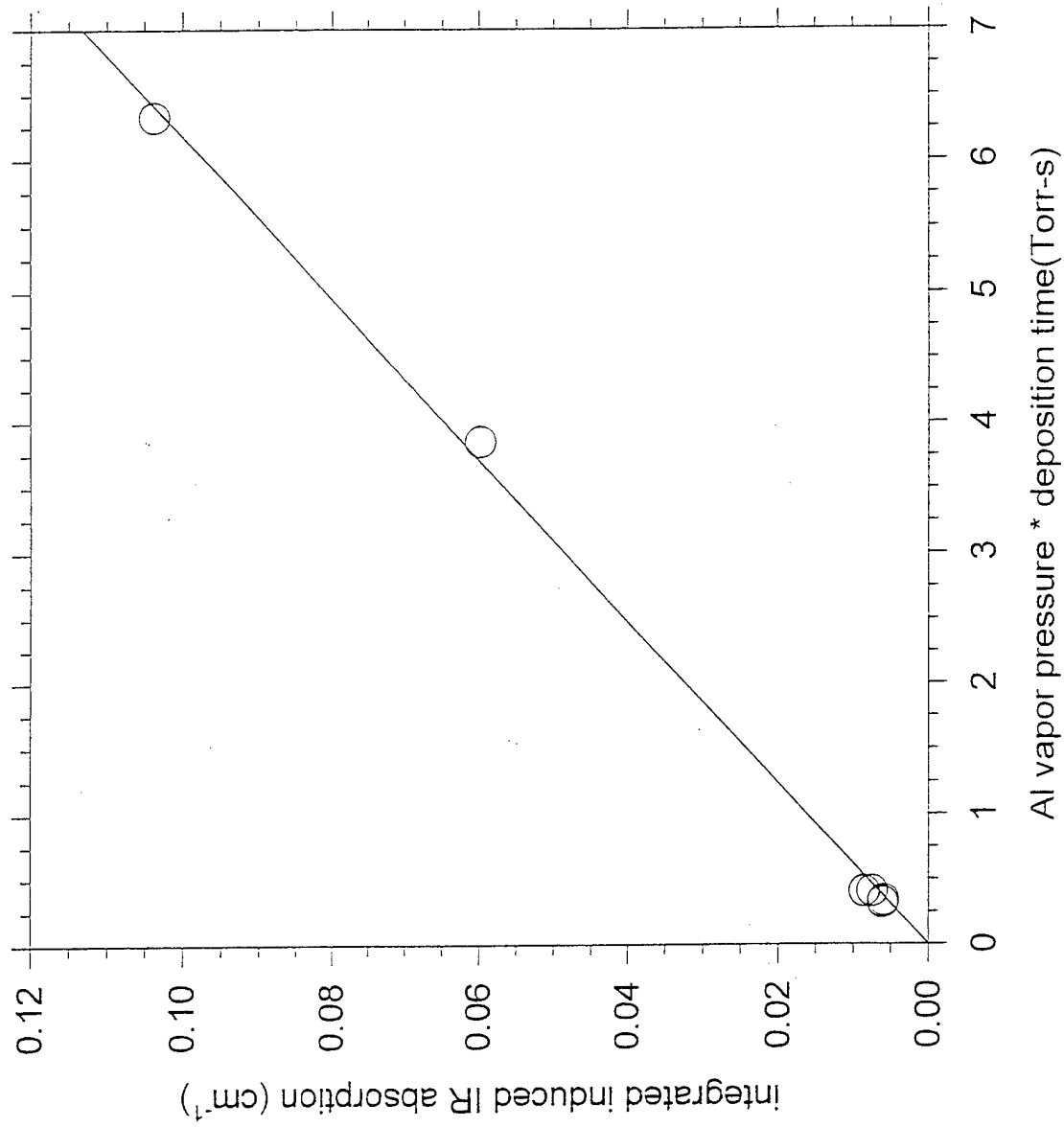


Analysis in collaboration with Prof. R.J. Hinde, U. Tennessee (Knoxville).

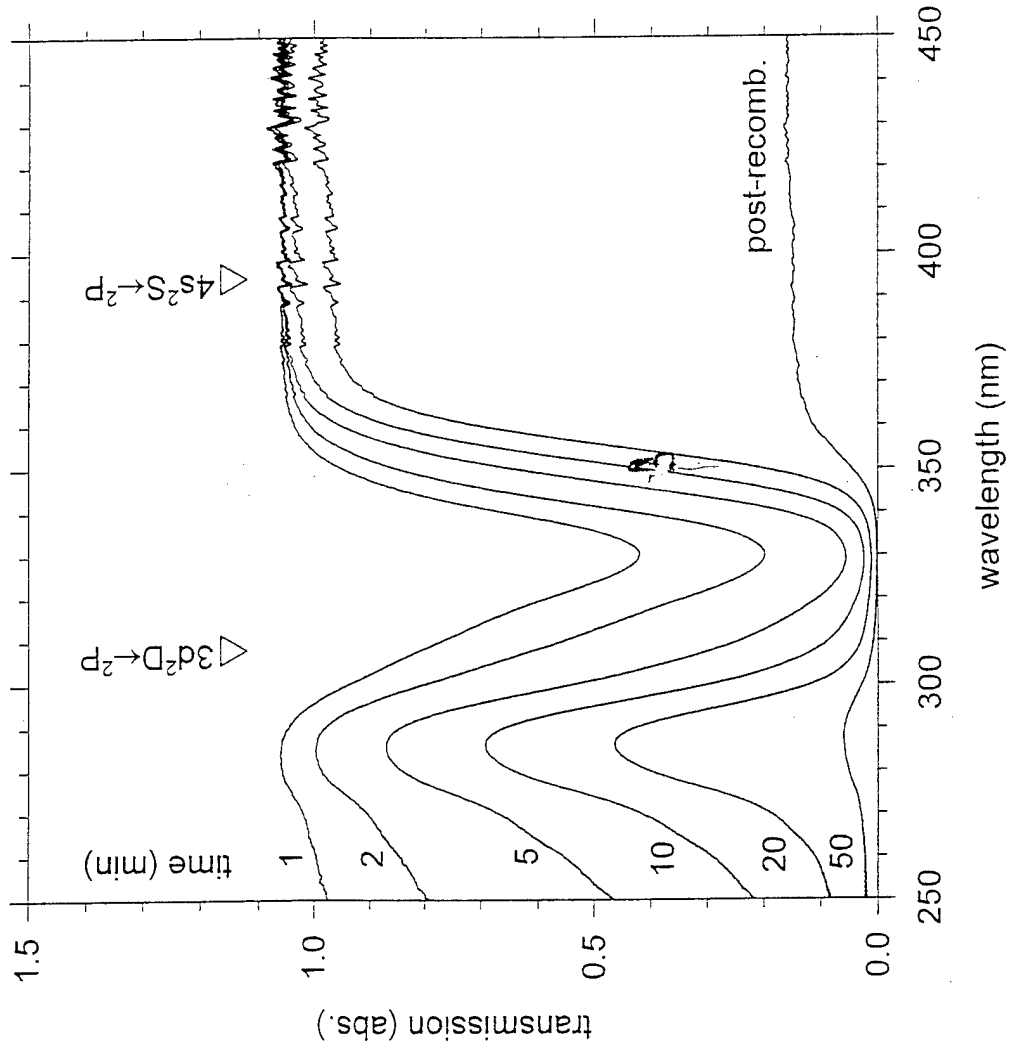
Correlation Between UV & IR Absorptions



Constant Al Atom Deposition Efficiency



UV Spectrum of Recombined Al/pH₂

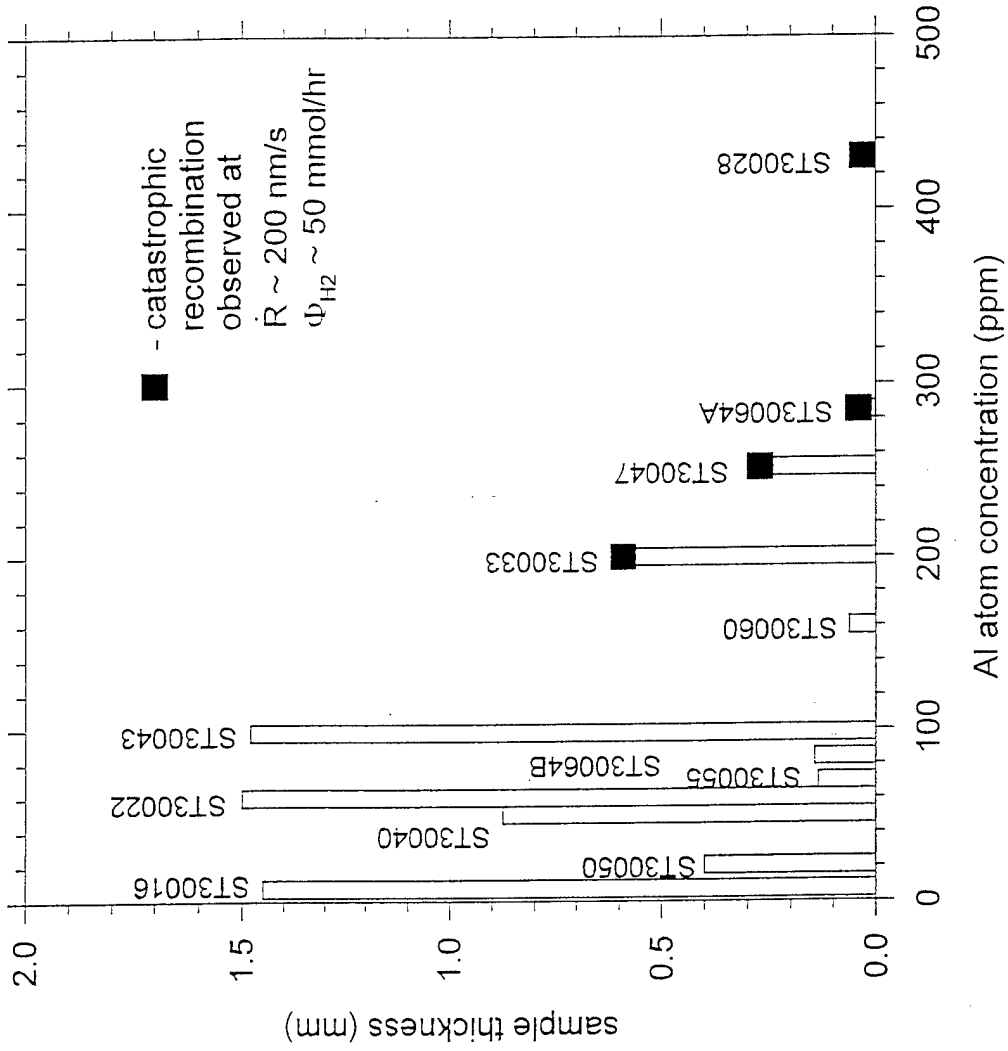


AFOSR Molecular Dynamics Contractors' Conference, Cryosolid Propellants Workshop, Irvine, CA, 20 May 2001.

Recombination/reaction in Al/pH_2

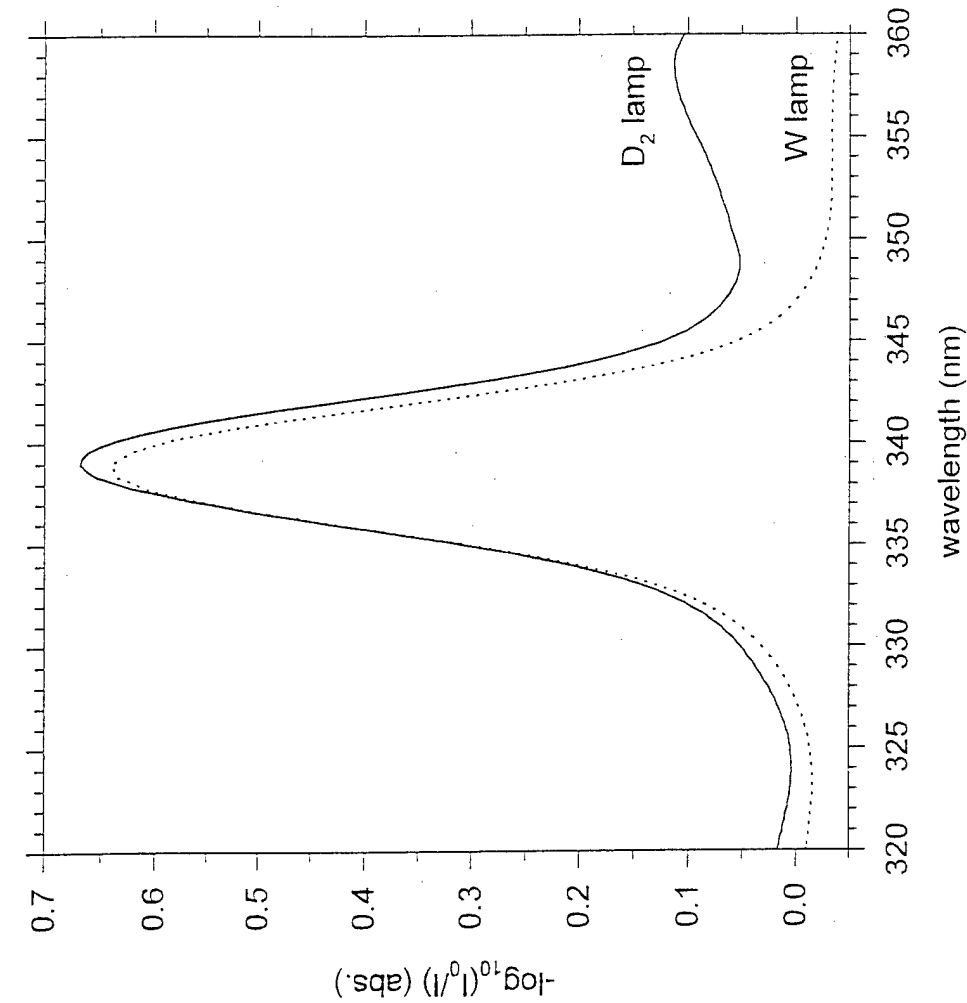


Summary of Al/pH₂ Deposition Results



1000 ppm Al/Ar

* Evaporate Al from 1 mm dia. Ta filaments



Al atoms in solid Ar

$$N_i = \frac{2.303 m_e c^2 \int A_{10} d\lambda}{\pi e^2 \lambda_0^2 f_{ik} d}$$

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

$$d = 4 \text{ } \mu\text{m}$$

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

$$C_{Al} = 0.1 \%$$

$$\Delta t = 13 \text{ min}$$

$$\Phi_{Al} = 1.5 \times 10^{13} \text{ \#/cm}^2\text{-s}$$

$$\textcircled{a} R = 5 \text{ cm}$$

Al/pH₂ Summary

- * Demonstrated trapping of ≈ 0.1 % Al atoms in thin Ar solids using home-made Al atom source.
- * Demonstrated Al-induced IR absorption by pH₂ 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 pH₂ solids failed, resulting in catastrophic recombination (and reaction?) of the Al atoms.
- * Interpretation: thick vapor deposited pH₂ solids impede dissipation of heat released upon atomic recombination, causing a recombination cascade. Attempt depositions of thin (~ 10 μm), high Al atom concentration Al/pH₂ samples (worked for Ar matrices).

Is Catastrophic Recombination Ubiquitous to Rapid Vapor Deposited pH_2 Solids?

$$* \quad \frac{1}{k_{\text{recomb}}} = \frac{1}{k_{\text{intrinsic}}} + \frac{1}{k_{\text{diff}}}$$

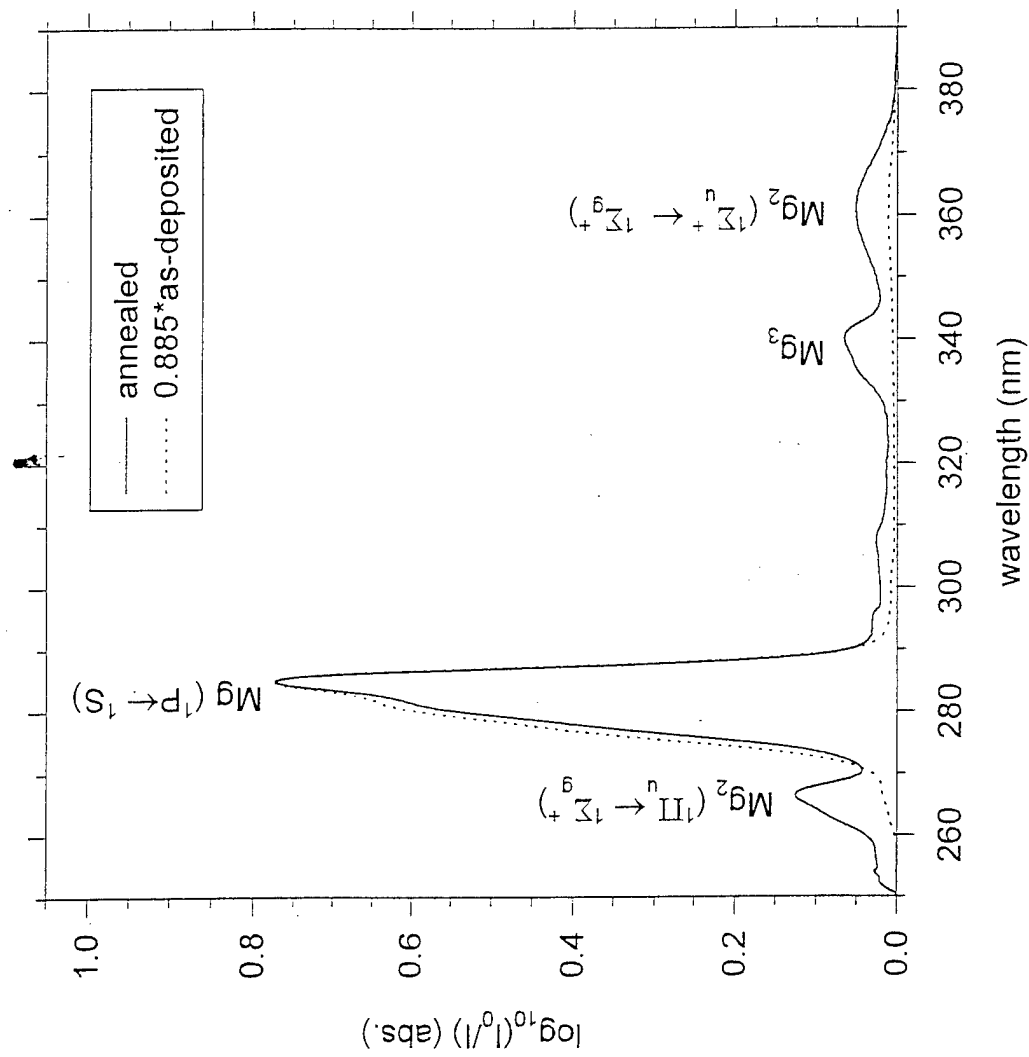
- * $k_{\text{intrinsic}}$ depends on M-M interaction potential, increases with increasing well depth and range
- * \Rightarrow try Mg atoms as "HEDM" dopant
Mg-Mg and Mg-Mg_n "van der Waals" interactions

M-M Diatomic Ground State Potentials

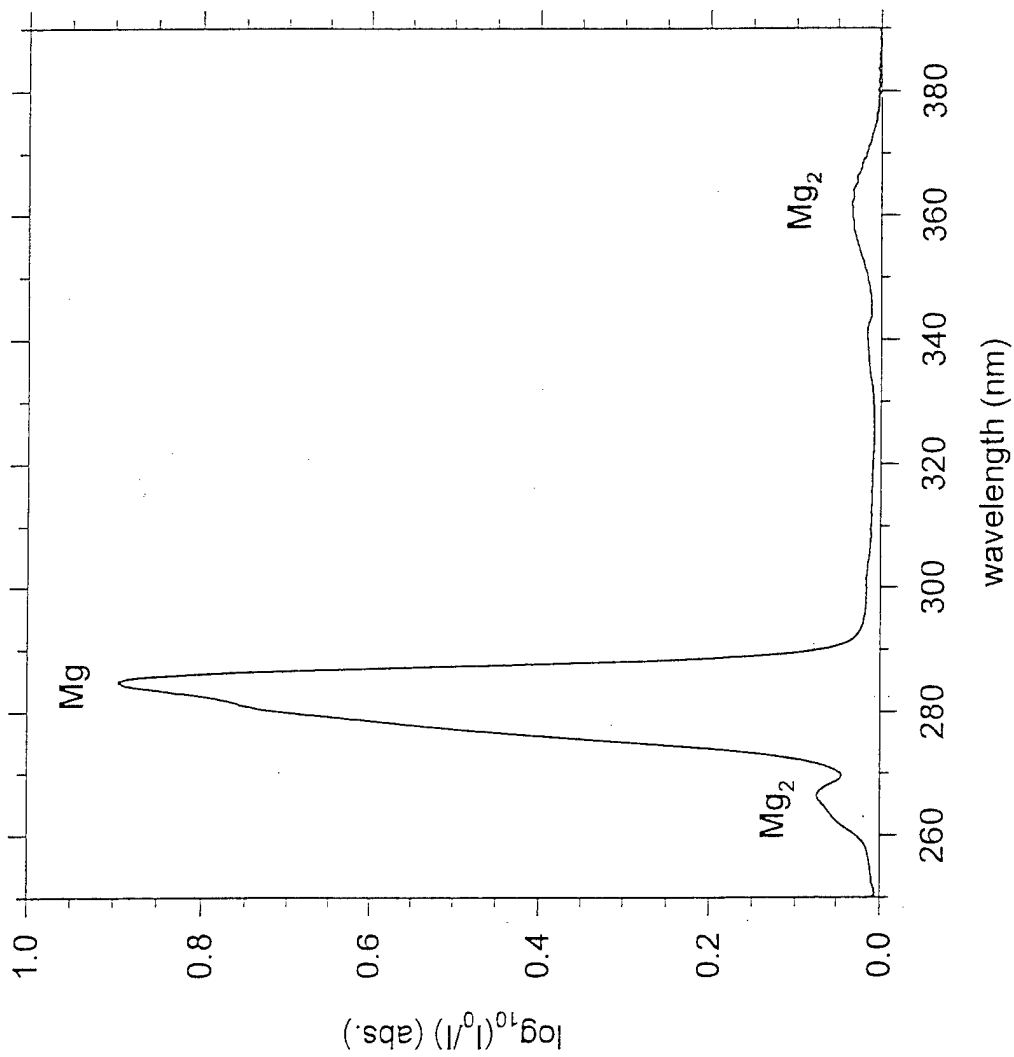
INCOMPLETE SLIDE

- * 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/pH₂ (d=0.07 mm)



As-Deposited 35 ppm Mg/pH₂ (d=0.02 mm)



Contractor Support of In-House Effort

- * Assignment of Al/pH₂ 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 pH₂ (?)
- * 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 $k_{\text{intrinsic}}$
 - Vary pH₂ deposition rate/sample thickness, and compare with Ne and Ar hosts to test k_{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 IHe II (ala Gordon)
 - In-Situ Photolysis of HEDM Precursors (Apkarian, Stwalley)
 - Open Discussion: other suggestions?

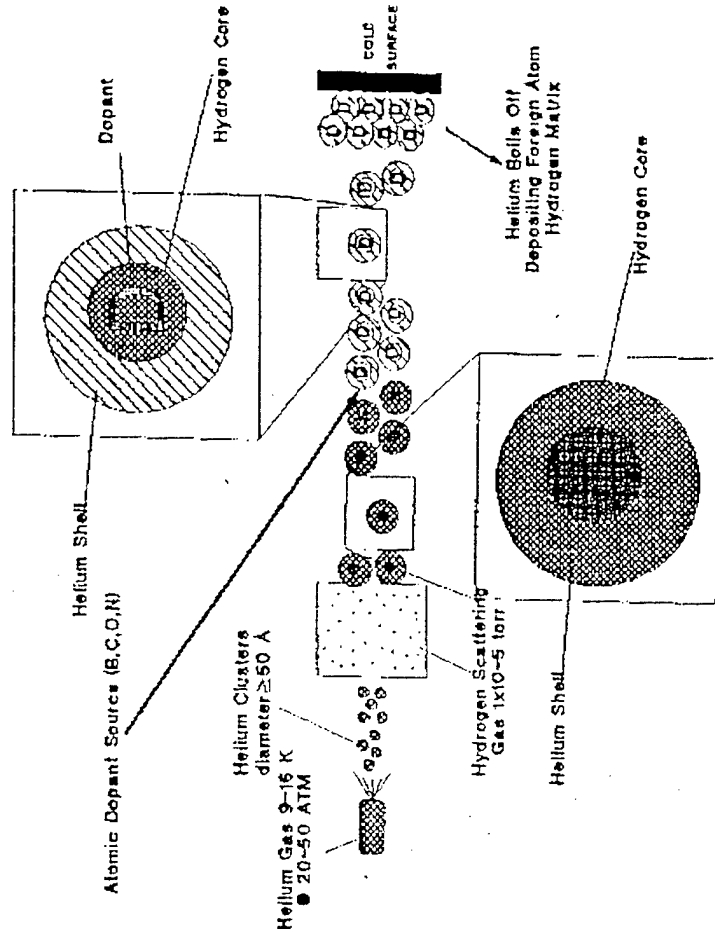
Future Direction: Cluster Deposition (?)

Toward the Production of Measurable Quantities of Highly Doped Solid Hydrogen

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

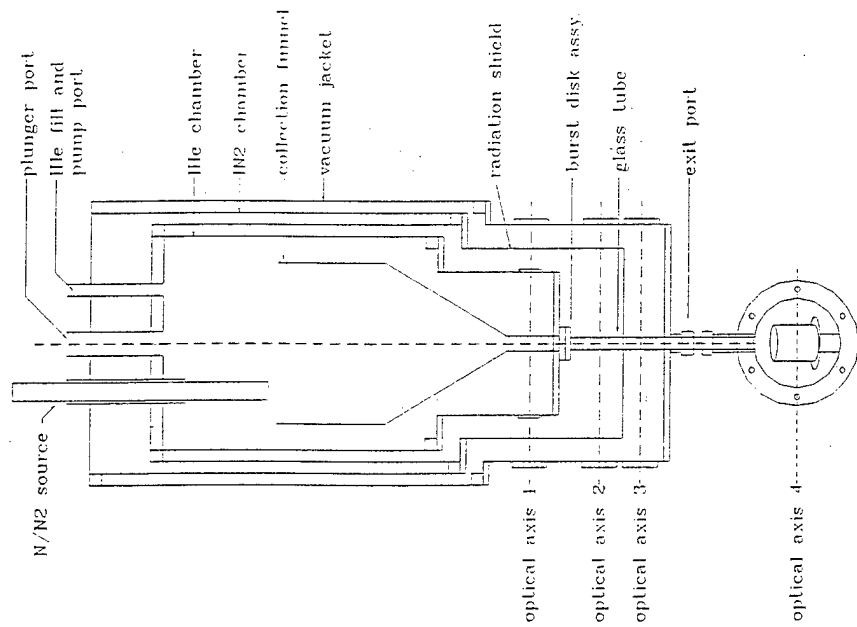
Berton Callicott, Kenneth C Janda, V. A. Apkarian, R. B. Gerber
Zhiming Li, P. Taborek and J. Rutledge
Advanced Cryogenic Materials Group
University of California
Irvine, California

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 Toennies¹ 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 IHe 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... (?)

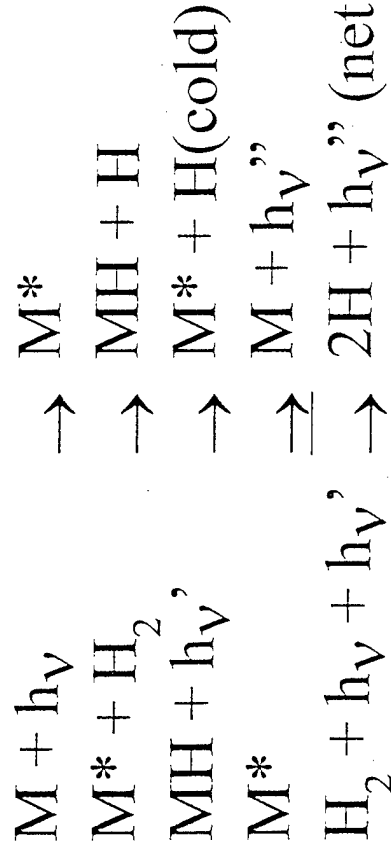
Future Direction: In-Situ Photolysis (?)

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



(5% O/H₂ ⇒ 25s (6%) I_{sp} improvement, so Al > O > H)
UV induced desorption of H₂O inside vacuum chamber
complicates monitoring O + H₂ reactions.

* W.C. Stwalley proposal (c1992):



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.